NMR EPR

1998
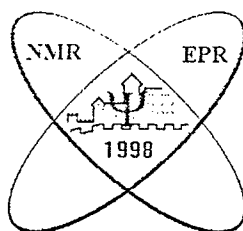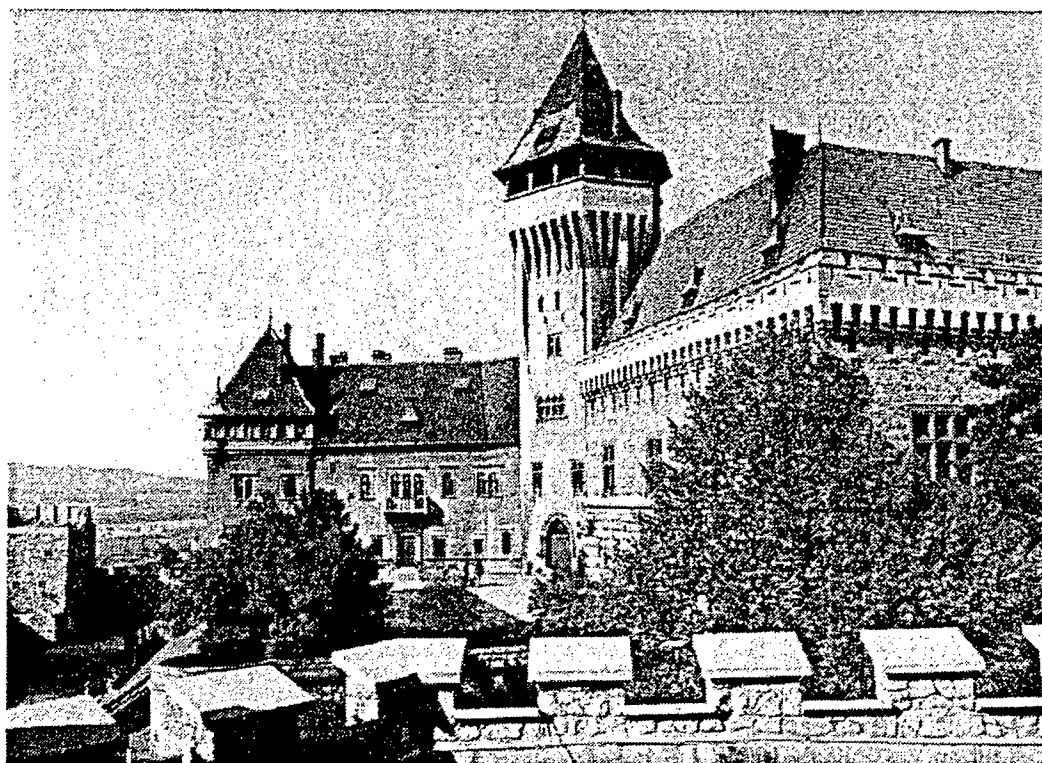
International Conference on:

Quantum Chemical Calculations of NMR and EPR Parameters

Castle Smolenice, Slovak Republic

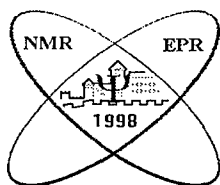## *September 14 - 18, 1998*

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 21 October 1998	3. REPORT TYPE AND DATES COVERED Conference Proceedings

4. TITLE AND SUBTITLE

Quantum Chemical Calculations of NMR and EPR Parameters

5. FUNDING NUMBERS

F61775-98-WE006

6. AUTHOR(S)

Conference Committee

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Max Planck Institute
Heisenbergstr. 1
Stuttgart D-70569
Germany

8. PERFORMING ORGANIZATION REPORT NUMBER

N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

EOARD
PSC 802 BOX 14
FPO 09499-0200

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

CSP 98-1045

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

A

13. ABSTRACT (Maximum 200 words)

The Final Proceedings for Quantum Chemical Calculations of NMR and EPR Parameters, 15 September 1998 - 19 September 1998

This is an interdisciplinary conference. Topics include issues and new methods in the theory and computational techniques involved in Nuclear Magnetic Resonance (NMR) and Electron Paramagnetic Resonance (EPR).

14. SUBJECT TERMS

EOARD, Quantum Chemistry, Nuclear Magnetic Resonance, Nuclear Magnetic Resonance, Magnetic Resonance Spectroscopy, Magnetic Resonance Spectroscopy, Electron Paramagnetic Resonance, Electron Paramagnetic Resonance

15. NUMBER OF PAGES

83

16. PRICE CODE

N/A

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

International Conference on:
Quantum Chemical Calculations of
NMR and EPR Parameters
Castle Smolenice, Slovak Republic
September 14 - 18, 1998

Sponsors

International Conference on:

Quantum Chemical Calculations of NMR and EPR Parameters
Castle Smolenice, Slovak Republic
September 14 - 18, 1998

Organizing Committee

V. G. Malkin (Chairman)

Institute of Inorganic Chemistry
Slovak Academy of Sciences
Dubravska cesta 9
SK-84236 Bratislava
Slovak Republic

M. Kaupp (Co-Chair)

Max-Planck Institut für
Festkörperforschung
Heisenbergstr. 1
D-70569 Stuttgart
Germany

International Scientific Committee

W. Kutzelnigg (Bochum, Germany)

J. Oddershede (Odense, Denmark)

P. Pyykkö (Helsinki, Finland)

W. T. Raynes (Sheffield, UK)

J. A. Tossell   (Maryland, USA)

Local Committee

E. Komorowska

O. L. Malkina

J. Noga

D. Tunega

V. G. Malkin (Chair)

A. Michalková

A. Pappová

L. Turi Nagy   (Secretary)

"Quantum Chemical Calculations of NMR and EPR Parameters"

Time	Monday 14.09	Time	Tuesday 15.9	Time	Wednesday 16.9	Time	Thursday 17.9	Time	Friday 18.9
					M. Kaupp		*P. Pyykkö*		*T. Ziegler*
		9:00	**OPENING**	9:00	R. E. Wasylishen	9:00	T. Ziegler	9:00	G. H. Lushington
			Award presentation	9:45	M. Bühl	9:45	S. M. Colwell	9:40	D. Jayatilaka
			W. Kutzelnigg						
		9:30	R. R. Ernst						
		10:30	**COFFEE**	10:20	**COFFEE**	10:20	**COFFEE**	10:20	**COFFEE**
			G. Frenking	10:40	U. Fleischer	10:40	L. Visscher	10:40	C. J. Jameson
		11:00	P. Pulay	11:15	H.-U. Siehl	11:15	O. Vahtras	11:15	H.-H. Limbach
		11:40	J. Gauss	11:50	G. Frenking	11:50	E. van Lenthe	11:50	D. R. Salahub
				12:25		12:25		12:25	
		12:30	*LUNCH*	12:30	*LUNCH*	12:30	*LUNCH*	12:30	*LUNCH*
			M. Jaszuński		*S. Lunell*				*R.J. Bartlett*
14:00	**REGISTRATION**	14:00	R. J. Bartlett	14:00	E. Roduner	14:00	*EXCURSION*	14:00	K. Schwarz
		14:45	K. Ruud	14:35	L. A. Eriksson		*AND*	14:35	H. Ebert
		15:20	P. Lazzeretti	15:10	B. Engels		*WINE TASTING*	15:10	F. Mauri
		15:55	**COFFEE**	15:45	**COFFEE**			15:45	**COFFEE**
		16:20	J. Weber	16:10	P. O'Malley			16:10	N. M. Sergeyev
		16:55	D. Chipman	16:45	P. M. Lenahan			16:45	W. T. Raynes
17:00	**MIXING PARTY**	17:30		17:15	S. P. Karna			17:20	*P. Pyykkö*
		17:40		17:40					*concluding remarks*
		18:00	**DINNER**	18:00	**DINNER**			18:00	**CLOSING**
		20:00	**POSTER**	20:00	**POSTER**	19:00	**BARBECUE**	19:00	**DINNER**
			SESSION		**SESSION**		**(BANQUET)**		

Program

Monday, Sept. 14, afternoon:

14:00 - 21:00 Registration open
17:00 Welcome mixer

Tuesday, Sept. 15, morning:

9:00   Opening
Presentation of the Medal of Dionýz Ilkovič to
Prof. Dr. Werner Kutzelnigg

9:30   *session chair: W. Kutzelnigg*
R. R. Ernst
Dynamical and Structural Studies of Molecules. NMR Experiments,
Quantum Chemistry, and Molecular Dynamics Simulation

10:20   Discussion

10:30   Coffee break

11:00   *session chair: G. Frenking*
P. Pulay
Parallel Calculation of NMR Shieldings on Clusters of Inexpensive
Computers: Applications to Peptides

11:35   Discussion

11:40   **J. Gauss**
Recent Developments in the Accurate Calculation of NMR Chemical
Shifts

12:15   Discussion

12:30   Lunch

Tuesday, Sept. 15, afternoon:

14:00   *session chair: M. Jaszuński*

R. J. Bartlett

The Coupled-Cluster Treatment of NMR and ESR Spectra

14:40   Discussion

14:45   **K. Ruud**

The MCSCF Response Approach to Relativistic Corrections to NMR Parameters

15:15   Discussion

15:20   **P. Lazzeretti**

On CHF Calculations of Second-Order Magnetic Properties Using the Method of Continuous Transformation of Origin of the Current Density

15:50   Discussion

15:55   Coffee break

16:20   **J. Weber**

A Density Functional Theory Based Scheme for Studying ESR and NMR Properties of Small Molecules Embedded in Larger Systems

16:50   Discussion

16:55   **D. M. Chipman**

New Quantum Mechanical Operators for EPR Hyperfine Coupling and NMR Spin-Spin Coupling Constants

17:25   Discussion

18:00   Dinner

20:00-
22:00   POSTER SESSION

Wednesday, Sept. 16, morning:

9:00   *session chair: M. Kaupp*

R. E. Wasylishen

Characterization of Nuclear Magnetic Shielding, Indirect Spin-Spin
Coupling and Electric Field Gradient Tensors using Solid-State NMR

9:40   Discussion

9:45   **M. Bühl**

Substituent Effects on Transition-Metal Chemical Shifts

10:15   Discussion

10:20   Coffee break

10:40   **U. Fleischer**

Calculations of Phosphorus Nuclear Magnetic Shielding Tensors

11:10   Discussion

11:15   **H.-U. Siehl**

Recent Advances in the Experimental and Computational
Characterisation of Carbocations

11:45   Discussion

11:50   **G. Frenking**

Theoretically Predicted ^{13}C NMR Chemical Shifts and C-C Coupling
Constants as Tools for the Conformational Analysis of Natural
Products. A DFT and Molecular Mechanics Study

12:20   Discussion

12:30   Lunch

Wednesday, Sept. 16, afternoon:

14:00   *session chair: S. Lunell*

E. Roduner

The Challenge of EPR Parameters

14:30   Discussion

14:35   **L. A. Eriksson**

Applicability of DFT and Hybrid HF-DFT Methods for Evaluating EPR Parameters in Bioradicals

15:05   Discussion

15:10   **B. Engels**

Ab initio Calculations of ESR Parameters

15:40   Discussion

15:45   Coffee break

16:10   **P. J. O'Malley**

Hyperfine Coupling Determination for Free Radical Intermediates of Photosynthetic Electron Transfer

16:40   Discussion

16:45   **P. Lenahan**

Paramagnetic Centers in Amorphous Insulating Films

17:15   **S. P. Karna**

Theory of Electric Field Effects on Hyperfine Interaction

17:35   Discussion

18:00   Dinner

20:00-
22:00   POSTER SESSION

Thursday, Sept. 17, morning:

9:00
session chair: P. Pyykkö

T. Ziegler

A GIAO-DFT Approach to the Calculation of NMR and ESR Parameters: Quantitative Results and Qualitative Interpretations

9:40
Discussion

9:45
S. M. Colwell

Density Functional Theory Calculations of Magnetic Properties: Improved Functionals and Current Dependence

10:15
Discussion

10:20
Coffee break

10:40
L. Visscher

Relativistic Calculations of the NMR Shielding and Indirect Spin-Spin Coupling Tensors

11:10
Discussion

11:15
O. Vahtras

Calculations of Electronic g-Shifts by Linear Response Theory for Multiconfigurational SCF Wave Functions

11:45
Discussion

11:50
E. van Lenthe

Density Functional Calculations of ESR Parameters in the Zero Order Regular Approximation for Relativistic Effects

12:20
Discussion

12:30
Lunch

Thursday, Sept. 17, afternoon:

14:00
Excursion and wine tasting

19:00
Conference dinner (barbecue)

Friday, Sept. 18, morning:

9:00   *session chair: T. Ziegler*

G. H. Lushington

Perspectives on ab initio g-Tensor Calculations

9:40   Discussion

9:45   **D. Jayatilaka**

Electron Spin Resonance g-Tensor Calculations

10:15   Discussion

10:20   Coffee break

10:40   **C. J. Jameson**

Application of Nuclear Shielding Surfaces to the Fundamental Understanding of Adsorption and Diffusion in Microporous Solids

11:10   Discussion

11:15   **H.-H. Limbach**

NMR Views of Proton Transfer and Hydrogen Bonding

11:45   Discussion

11:50   **D. R. Salahub**

SOS-DFPT (deMon-NMR) Calculations for Enzyme and Zeolite Models

12:20   Discussion

12:30   Lunch

Friday, Sept. 18, afternoon:

14:00   *session chair: R. J. Bartlett*

K. Schwarz

Electric Field Gradients in Solids by the Full-Potential LAPW Method

14:40   Discussion

14:45   **H. Ebert**

A Fully Relativistic Description of the Hyperfine Interaction in Solids

15:15   Discussion

15:20   **F. Mauri**

Ab-initio Theory of the NMR Chemical Shifts in Solids and Liquids

15:50   Discussion

15:55   Coffee break

16:20   **N. M. Sergeyev**

The Isolated Water Molecule. New Experimental and Theoretical Data

16:50   Discussion

16:55   **W. T. Raynes**

Isotope Effects on the NMR Parameters of Water Calculated from Correlated Nuclear Shielding and Nuclear Spin-Spin Coupling Surfaces

17:25   Discussion

17:30   **P. Pyykkö**

Concluding remarks

18:00   Closing dinner

Saturday, Sept. 19: Departure

ABSTRACTS

OF

LECTURES

Dynamical and Structural Studies of Molecules. NMR Experiments, Quantum Chemstry, and Molecular Dynamics Simulation.

R.R.Ernst, T. Bremi, R Brueschweiler, S.Lienin, R.Meyer, P.Robyr, Ch.Scheurer, and M.Utz

Laboratorium fuer Physikalische Chemie, ETH-Zentrum, 8092 Zurich, Switzerland

NMR experiments provide unique insights into structural features and particularly into dynamical aspects of molecules. Chemical shift, J-coupling, and relaxation measurements using sophisticated experimental techniques form the basis of the exploration. The analysis of the data requires a detailed knowledge of the underlying structural dependence of the NMR parameters. Rarely they can be measured with sufficient accuracy. Often, they need to be calculated by quantum chemical methods. The interpretation of the intramolecular dynamics can take advantage of computer modelling by molecular dynamics simulations.

Examples that combine NMR experiments, quantum chemical calculations, and molecular dynamics simulations are presented. They involve intra-molecular dynamics of peptides and proteins, hydrogen dynamics in transition metal hydrides, and the interpretation of local order in amorphous polymers.

Parallel Calculation of NMR Shieldings on Clusters of Inexpensive Computers: Applications to Peptides

Peter Pulay

Department of Chemistry ad Biochemistry

Fulbright College of Arts ad Sciences

University of Arkansas, Fayetteville, Arkansas

Strategies for efficient parallelization of ab initio NMR shielding computations at the SCF and DFT level will be discussed, with emphasis on clusters of inexpensive computers. Such a cluster can give supercomputer performance at a very moderate price, opening new possibilities for the computational approach. Calculations with 500-1000 basis functions can be routinely performed. Large-scale calculations for peptide shielding surfaces, and for polysilanes will be described.

RECENT DEVELOPMENTS IN THE ACCURATE CALCULATION OF NMR CHEMICAL SHIFTS

Jürgen Gauss

Institut für Physikalische Chemie,
Universität Mainz, D-55099 Mainz, Germany

Recent developments for the accurate calculation of NMR chemical shifts using many-body perturbation theory (MBPT) and coupled-cluster (CC) methods will be discussed. In particular, we will present

- CC calculations for a series of small diatomic molecules together with a treatment of rovibrational corrections and temperature effects,

- a chemical application (to a substituted vinyl cation) where only high-level coupled-cluster calculations resolve an earlier discrepancy between theory and experiment,

- a recent integral-direct implementation at the second-order MBPT level which allows electron-correlated NMR chemical shift calculations on large molecules with more than 50 atoms.

THE COUPLED-CLUSTER TREATMENT OF NMR AND ESR SPECTRA

Rodney J. Bartlett, Ajith Perera, Janet Del Bene, Tom Henderson
Quantum Theory Project
University of Florida
Gainesville, FL, USA 32611

Hydrogen bonds are ubiquitous in chemistry and biochemistry, being essential to life itself. However, the concept of a hydrogen bond in biochemistry consists solely of a double well potential, regardless of the atoms and circumstances involved in the bond. Consequently, NMR spectra for biomolecules are invariably interpreted subject to this underlying model of an H-bond. We will present studies of NMR chemical shifts and coupling constants for a variety of H-bonds demonstrating that different H-bonds have characteristic NMR spectra that can be used for their identification and detection. We also consider coupling constants in polypeptides, presenting purely *ab initio* Karplus-type relations for the conformations of peptide units.

In ESR we consider the determination of hyperfine coupling constants for quinones, using the relaxed density-matrix approach of coupled-cluster theory.

The MCSCF response approach to relativistic corrections to NMR parameters

Kenneth Ruud[1], Juha Vaara[2], Olav Vahtras[3], Boris F. Minaev[3], Hans Ågren[3], and Jukka Jokisaari[2]

[1] Department of Chemistry, University of Oslo, P.O.Box-1033 Blindern, N-0315 Oslo, Norway

[2] NMR Research Group, Department of Physical Sciences, University of Oulu, P.O.Box 333, FIN-90571 Oulu, Finland

[3] Department of Physics and Measurement Technology, Linköping University, S-58183 Linköping, Sweden

The talk will outline the recent progress that has been made in the calculation of relativistic corrections to nuclear magnetic resonance parameters using linear and quadratic MCSCF response theory. The talk will briefly discuss the theory, with emphasis on the computational strengths and weaknesses.

The main part of the talk will be devoted to presenting results of recent MCSCF calculations of the spin–orbit corrections to the nuclear shielding and indirect spin–spin coupling constants for different molecules. Some of these studies have utilized large basis sets and large active spaces, providing benchmark results for small molecules which may be used for calibrating more approximate treatments of the relativistic effects.

The internuclear distance dependence of the nuclear shieldings and the spin–orbit corrections to the nuclear shieldings will also be discussed.

ON CHF CALCULATIONS OF SECOND-ORDER MAGNETIC PROPERTIES USING THE METHOD OF CONTINUOUS TRANSFORMATION OF ORIGIN OF THE CURRENT DENSITY

S. Coriani, P. Lazzeretti, M. Malagoli and R. Zanasi,
Dipartimento di Chimica, Università degli Studi,
via G. Campi 183, 41100 Modena, Italy.

Abstract

A fully analytical formulation is outlined for computing molecular magnetic susceptibilities and nuclear magnetic shieldings via a continuous change of origin of the electronic current density induced by an external magnetic field. The change of origin is described in terms of a (continuous) arbitrary shift function $d(r)$. Coupled Hartree-Fock second-order magnetic properties of CH_4 and CO_2 molecules have been computed, using the special choice $d(r)= r$ as generating function. A detailed analysis of results obtained with a variety of basis sets reveals that such a method is not as good as previously suggested. Large basis sets must be used to obtain accurate magnetic properties. On the other hand, all the components of theoretical nuclear magnetic shielding evaluated via this approach are independent of the origin of the vector potential. In general, theoretical magnetic susceptibilities depend linearly on the distance between different coordinate frames, but are origin independent for centre-symmetric molecules.

A Density Functional Theory based scheme for studying ESR and NMR properties of small molecules embedded in larger systems.

Jacques Weber and Tomasz Adam Wesolowski
Département de Chimie Physique, Université de Genève,
30, quai Ernest-Ansermet, CH-1211 Genève 4, Switzerland

A theoretical formalism for studying properties of molecules embedded in larger systems is presented. This method (Kohn-Sham Equations with Constrained Electron Density [1-3], KSCED) is based on a modification of the standard method of Kohn and Sham. As a consequence of partitioning the total electron density into two components ($\rho = \rho_1 + \rho_2$), an additional functional is used to approximate a small fraction of the total kinetic energy ($T_s^{nad} [\rho_1, \rho_2] = T_s[\rho_1 + \rho_2] - T_s[\rho_1] - T_s[\rho_2]$).

We started combining KSCED with approaches developed recently by Malkin et al [4] for calculating NMR and ESR properties using density functional theory. Our present paper will presents the first results obtained using this new methodology:
a) the influence of the Ar or Ne matrix on the hyperfine coupling constant of Mg^+, b) the effect of interactions with different cations on the CO_2^- hyperfine coupling constants. The calculated properties are in excellent agreement with experimental results.

[1] T.A.Wesolowski and A.Warshel (1993) J. Phys. Chem., **97**, 8050
[2] T.A.Wesolowski and J.Weber (1996) Chem.Phys.Lett, **248**, 71
[3] T.A.Wesolowski (1997) J. Chem. Phys., **106**, 8516
[4] V. Malkin, O.L. Malkina, L.A. Eriksson, and D.R. Salahub, in "Theoretical and Computational Chemistry" vol. 1, "Density Functional Calculations" P. Politzer and J.M. Seminario, Eds., Elsevier, 1995

NEW QUANTUM MECHANICAL OPERATORS FOR EPR HYPERFINE COUPLING AND NMR SPIN-SPIN COUPLING CONSTANTS

Daniel M. Chipman
Radiation Laboratory, University of Notre Dame
Notre Dame, IN 46556 USA

and

Vitaly A. Rassolov
Department of Chemistry, Northwestern University
Evanston, IL 60208 USA

New global operators have been derived to express the Fermi contact interaction between an electron and a nucleus or between two electrons. These supply a useful alternative to the traditional representation in terms of a delta function operator. Among their interesting formal properties are proper cusp behavior of the density even when the underlying wave function is cuspless, such as is the case with Gaussian basis sets. Certain serious difficulties known for the behavior of the global operator previously introduced by Hiller, Sucher, and Feinberg, such as improper long range asymptotic behavior and very inefficient implementation due to contributions from two-electron integrals, are ameliorated in the new formulations.

Practical results using the new operators are presented for difficult properties such as first-order hyperfine coupling constants, as observed in EPR, and second-order indirect nuclear spin-spin coupling constants, as observed in NMR. Compared with the traditional delta function formulations, insignificant additional computer time is required to carry out these calculations. It is found that the new operators can give higher accuracy from medium sized basis sets, and also faster convergence to the complete basis set limit.

Characterization of Nuclear Magnetic Shielding, Indirect Spin-Spin Coupling and Electric Field Gradient Tensors using Solid-State NMR.

Rod Wasylishen, G. Bernard, D. Bryce, K. Eichele, M. Gee, M.D. Lumsden, S. Kroeker, G. Ossenkamp, R. Schurko, G. Wu.

*Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J3.*

Solid-state NMR is ideally suited for probing the orientation dependence of magnetic shielding, spin-spin coupling and EFG tensors. NMR studies of single crystals provide the most definitive information about these NMR tensors. In the case of powder samples, it is advantageous to examine systems where the crystal symmetry guarantees that the NMR parameters will be axially symmetric. Several examples demonstrating the utility of solid-state NMR will be provided. For example, nitrogen shielding tensors of aniline-^{15}N and pyridine-^{15}N cobaloximes; phosphorus shielding tensors for cis- and trans-substituted diphosphetes, Cu, P spin-spin coupling tensors for Cu(I)-phosphine complexes, aluminium shielding and EFG tenors for several nearly octahedral complexes, etc. The importance of first principle calculations will be discussed and several challenging problems will be presented.

SUBSTITUENT EFFECTS ON TRANSITION-METAL CHEMICAL SHIFTS.

M. Bühl

Organisch-Chemisches Institut, Universität Zürich, Winterthurerstr. 190,
8057 Zürich, Switzerland

Chemical shifts of transition-metal nuclei in a large number of bonding situations can be well reproduced with modern tools of density-functional theory.[1] Effects of substituents in the first and second coordination sphere can be rationalized, e.g. in terms of geometrical and electronic effects, and the parameters governing the observed trends can be identified. For rhodium complexes bearing chelate ligands, for example, it is shown that the Rh-ligand distance has a much larger effect on $\delta(^{103}Rh)$ than the chelate bite angle, hitherto assumed to be of prime importance.[2] The computed coordination geometry and ^{51}V chemical shift of the vanadate-glycylglycine complex below, modeling biologically relevant vanadate-peptide interactions,[3] is indicated to be quite sensitive to the pH value.

$\delta(^{51}V)_{calc}$ -502 ppm   -602 ppm   ≡ glygly
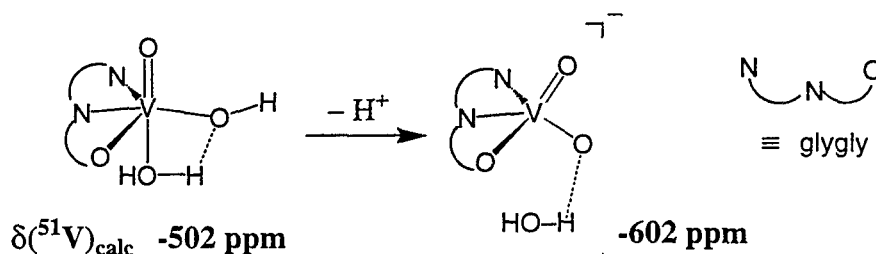
1. M. Bühl, M. Kaupp, V. G. Malkin, O. L. Malkina, *J. Comput. Chem.*, submitted.
2. e.g. J. G. Donkervoort, M. Bühl, C. J. Elsevier, *Eur. J. Inorg. Chem.*, submitted.
3. H. Sigel, A. Sigel, Eds., *Metal Ions in Biological Systems*, *Vol. 31*, Marcel Dekker, New York, 1995.

Calculations of Phosphorus Nuclear Magnetic Shielding Tensors

Ulrich Fleischer

Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas, 72701, USA – Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, FR Germany

The nuclear magnetic shielding of a nucleus is a sensitive probe of its local environment. In addition to the isotropic value the nuclear magnetic shielding tensors contain some spatially resolved information and are thus even more sensitive probes. We discuss results of our shielding tensor calculations on phosphorus compounds. Phosphorus has not only favourable NMR properties, it is also able to form bonds in a variety of different situations, from lowvalent multiple bonded up to hypervalent species.

Electron correlation effects are more pronounced for the lowvalent systems. HF-, DFT- and MP2-data of a few systems are presented and discussed.

Some of the calculational approaches allow for a breakdown of the calculated tensors into contributions of localised orbitals. The different orientations of the principal axes system and the variations of the principal values on substitution are discussed in terms of interactions of occupied and virtual orbitals induced by the external magnetic field.

To study the influence of intermolecular interactions on the shielding tensors calculations on clusters were performed. The structures were chosen to model the local environment of a molecule in the crystal. The results are discussed and compared to solid state NMR data.

Recent Advances in the Experimental and Computational Characterisation of Carbocations.

Hans-Ullrich SIEHL

University of ULM, Division of Organic Chemistry I
D-89069 ULM, Germany
e-mail: ullrich.siehl@chemie.uni-ulm.de, FAX +49-(0)731-502 2800

Carbocation chemistry has always been a cornerstone of physical organic chemistry and a test field for new experimental methods. Recently quantum chemical methods for the calculations of experimentally observable parameters such as chemical shifts and spin-spin coupling constants have become available. This has been a major breakthrough for the structure determination of reactive intermediates. We have applied the combination of contemporary experimental high field NMR methods and ab initio calculations to the investigation of new carbocations which shed some new light on controversial problems and demonstrate the fruitful interplay between experiment and theory.

Among others we will present H,C Cosy NMR spectra of silyl-substituted hypercoordinated bicyclobutonium cations and accompanying quantum chemical calculations of geometries and NMR chemical shifts and coupling constants.
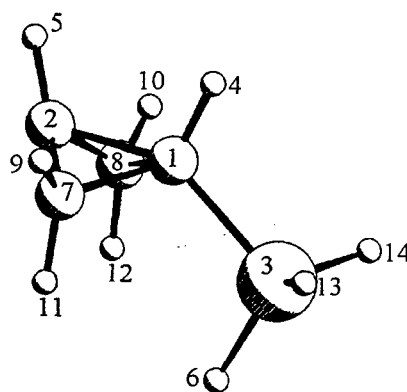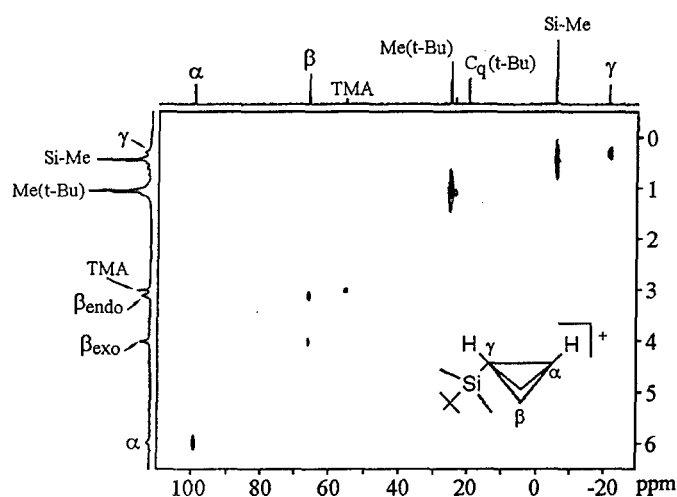
Theoretically predicted ^{13}C NMR Chemical Shifts and C-C Coupling Constants as Tools for the Conformational Analysis of Natural Products. A DFT and Molecular Mechanics Study

Gernot Frenking

*Fachbereich Chemie, Philipps-Universität Marburg,
Hans-Meerwein-Strasse, D-35032 Marburg, Germany*

The talk will focus on the scope and limits of a theoretical approach using Boltzmann weighted low-energy conformations given by molecular mechanics in conjunction with SOS-DFPT/IGLO calculated ^{13}C NMR chemical shifts and $^{3}J_{CC}$ coupling constants for the conformational analysis of polyketide natural products.

The Challenge of EPR Parameters

Emil Roduner

Institute of Physical Chemistry, University of Stuttgart,
Pfaffenwaldring 55, D-70569 Stuttgart

The predictability of hyperfine coupling constants of small organic free radicals has reached a level where quantum chemical calculations are very useful in assisting assignments of experimental values to chemical structures. However, running times become quickly prohibitive for a meaningful analysis of larger systems, or when temperature dependencies require extensive averaging over vibrational wave functions.

Transition metals play an important role in the chemistry of molecular complexes, in processes essential to life, and in catalysis. Since the metal centres are often paramagnetic, EPR becomes the method of choice for their investigation. g-tensor anisotropies are highly sensitive to the environment, hyperfine anisotropies and Fermi-contact interactions reflect the distribution of spin densities. The interpretation of these parameters, however, is far too often still persued on an empirical or intuitive level. Rigid quantum chemical methods which include electron correlation and relativistic effects seem to be on the horizon and are badly needed to assist the experimentalist.

Experimental results on temperature dependent hyperfine couplings, on g- and hyperfine tensors of transition metal ions and small clusters, and on ions interacting with an organic radical will be reported. Their structures and location in a zeolite lattice are expected to have tremendous impact on their catalytic activity and selectivity. Theoretical support is needed towards a detailed understanding of the observations.

Applicability of DFT and Hybrid HF-DFT Methods for Evaluating EPR Parameters in Bioradicals

Leif A. Eriksson
Dept. of Quantum Chemistry
Uppsala University
Box 518, 751 20 Uppsala, Sweden.
Email: leifaxel@kvac.uu.se

There is now growing evidence that radicals play a crucial role in several important enzymatic reaction mechanisms, both in terms of "storage units" for enzyme reactivity as well as being directly involved in reaction catalysis and/or control. During the last few years, the development of hybrid and gradient corrected density functional theory (DFT), coupled with new hardware technologies, have made accurate computational studies of these types of systems a feasible complementary tool to experiments.

In the present seminar, the free radical governed enzymatic reaction mechanism of Ribonucleotide Reductase (RNR) is outlined, based on theoretical calculations at the B3LYP level. In the deoxyribonucleotide generating protein the radical reactivity is kept "stored" at a diiron-linked tyrosine residue some 35 away from the active site. We outline the role of the tyrosine radical, the internal radical transfer, the radical catalyzed RNA to DNA conversion, and an alternative reaction mechanism observed upon subjecting the protein to a modified azido-substituted substrate, leading to destruction of the enzymatic function and reactivity.

Several examples will also be presented of other bioradicals, and how the EPR parameters evaluated at various DFT levels can serve as an aid for experimental interpretation and design of new models. We will in this section focus on DNA and sugar radicals generated upon exposure of DNA to ionizing radiation, and quinone radicals involved in photosynthesis in green plants and blue-green algae. Results obtained by combining DFT and molecular dynamics simulations will also be presented.

Ab initio calculations of ESR parameters

B. Engels, Inst. für Phys. und Theor. Chemie
University of Bonn, 53115 Bonn, Germany

To obtain accurate ESR parameters an accurate description of electron correlation is essential, making configuration interaction (CI) or other high level approaches mandatory in the case of ab initio calculations. On the other hand during the past few years it has been shown that density functional theory (DFT) gives also accurate ESR parameters in many cases, so that DFT became a serious alternative to conventional approaches. In the first part of this contribution the accuracy of DFT is compared with methods which combines CI methods with perturbational corrections. New developments in the individually selecting MR-CI method will be outlined.

The second part will be devoted to the influence of the nuclear dynamic on ESR parameters.

HYPERFINE COUPLING DETERMINATION FOR FREE RADICAL INTERMEDIATES OF PHOTOSYNTHETIC ELECTRON TRANSFER

P.J O'Malley

Department of Chemistry, UMIST, Manchester, M60 1QD, UK.

Free radicals of quinones, chlorophyll and tyrosine are formed in the initial electron transfer reaction of photosynthesis. Experimental determination of hyperfine couplings using EPR/ENDOR is difficult due to the broadened spectra observed for the immobilised species involved. We have recently had success in the quantitative prediction of isotropic and anisotropic hyperfine couplings using hybrid density functional calculations(1,2). These are proving to be an invaluable aid in the assignment of experimental spectra. Examples illustrating the application of the B3LYP density functional method to the calculation of spin densities and hyperfine couplings for semiquinone, tyrosyl and bacteriopheophytin radicals will be presented.

REFERENCES

1. P.J O'Malley, Density functional calculated 13-C, 17-O and 1-H isotropic and anisotropic hyperfine couplings for the plastosemiquinone anion radical involved in oxygenic photosynthesis, J. Amer. Chem. Soc., 1998 , 120, 5093

2. P.J O'Malley, Effect of hydrogen bonding on the spin density distribution and hyperfine couplings of the p-benzosemiquinone anion radical in alcohol solvents: A hybrid density functional study J. Phys. Chem. A, 1997, 101, 9813

Paramagnetic Centers in Amorphous Insulating Films

P.M. Lenahan
The Pennsylvania State University, University Park, PA 16802

Microelectronic technology is dominated by metal/oxide/silicon (MOS) integrated circuitry. Advances in MOS technology involve a continuous decrease in the dimensions of the individual devices which make up these integrated circuits. With device oxides of less than 5 nm in production today, the technology approaching fundamental physical limits. Point defects in amorphous insulating films and at amorphous film/silicon interfaces play important roles in these physical limitations. These defects already play important, not always deleterious, roles in the operation of present day devices. These point defects have been studied with electron paramagnetic resonance (EPR). EPR studies in these systems are fairly difficult. If the films studied are technologically useful, the defect densities are usually fairly low. Since the films are quite thin, one typically deals with small volumes of low defect density material. Although these difficulties have somewhat hampered work in this area, about twenty paramagnetic centers have been identified in these systems. Combinations of "electrical" and magnetic resonance measurements have identified the "electrical" properties of most of these centers. My presentation will review this work.

THEORY OF ELECTRIC FIELD EFFECTS ON HYPERFINE INTERACTION

Shashi P. Karna
Air Force Research Laboratory
Space Electronics and Protection Branch
3550 Aberdeen Ave, SE
Kirtland AFB, NM 87117-5776

The hyperfine splitting in the electron spin resonance (ESR) spectrum of a paramagnetic species experiences a linear shift in the presence of an external electric field, provided the magnetic nucleus is located at a noncentrosymmetric site. The electric-field-induced linear shift is also observed in the hyperfine splitting of nuclear quadrupole resonance (NQR) spectrum of a nucleus located at a noncentrosymmetric site in a molecule or in crystal lattice. Thus, the linear electric field effect on the ESR and NQR hyperfine splitting provide valuable information about the local atomic arrangement around a magnetic nucleus. The magnitude of the shift depends on the strength of interaction between the electron spin (charge) distribution and the external magnetic field, thus providing information about the spin (charge) distribution in the system.

The higher-order electric-field effects are not generally observed because of their decreasing magnitude. However, these effects could become important and observable when external electric field is due to high power laser.

This paper will discuss a perturbation theory treatment of the electric field effects on ESR and NQR hyperfine couplings. Theoretical methods to calculate the electric field effects within Hartree-Fock approach will be described. In order to illustrate the applicability and relevance of the theory, a few examples from the *ab initio* calculations of the first-order effects in selected molecules and radicals will be presented.

A GIAO-DFT Approach to the Calculation of NMR and ESR Parameters: Quantitative Results and Qualitative Interpretations:

Georg Schreckenbach, Yosadara Ruiz-Morales, Stephen K. Wolff and Yang Kahndogin, Sergei Patchkovskii and Tom Ziegler . Department of Chemistry, University of Calgary,Calgary,Alberta, Canada T2N 1N4.

We present new implementations and applications based on the ADF (Amsterdam Density Functional program system) GIAO-DFT scheme for the calculation of NMR[1a-c] and ESR[2a] shifts and spin-spin coupling constants[3a]. Results will be presented from shift calculations based on a new implementation that includes spin orbit-coupling[1d] and a fully relativistic treatment[1e] within the Zero-Order-Regular-Approximation[4]. The GIAO scheme in general lends itself well to qualitative interpretations. This will be demonstrated in connection with calculations on organic, inorganic and organometallic [77]Se[4a] and [125]Te[4b] shifts as well as coordination shifts of hydride[4c], CO[4d-e], and phosphine[4f] ligands attached to a metal fragment.

The second part deals with the calculation[2b] of metal-ligand NMR spin coupling constants as well as g-tensors of small radicals. It will be shown that environmental effects from the host lattice are important in g-tensor calculations[3b] and that better relativistic methods are required for NMR spin coupling constants involving 5d-elements. An account of our NMR and ESR work has appeared[6].

References:
1.(a) G.Schreckenbach and T.Ziegler **J.Phys.Chem.** 1995,99,606 (b)Schreckenbach, Georg. and Ziegler, Tom. **Int. J. Quant. Chem.** 1996,69,753-766 (c) G.Schreckenbach and T.Ziegler **Int. J. Quant. Chem.** 1997,61,899. (d) Wolff,S. and Ziegler,T. **J.Chem.Phys.** 1998. (e) Wolff,S. and Ziegler,T. **J.Chem.Phys.** sunmitted.
2. (a)Georg Schreckenbach and Tom Ziegler. **J.Phys.Chem A.** 1997,101,3388. (b) Patchkovskii,S.; Ziegler,T. work in progress.
3. (a) Dickson, Ross M., and Tom Ziegler. **J.Phys.Chem.** 1996,100,5286. (b) Kahndogin,J. and Ziegler.T. **Spec.Chem.Acta**, in press. (c) Kahndogin,J. and Ziegler.T, work in progress.
4. van Lenthe,E.; Baerends,E.J. and Snijders,J.G. J.Chem.Phys. 1993,99,4597.
5. Schreckenbach, Georg, Yosadara Ruiz-Morales, and_Tom Ziegler. **J.Chem.Phys** 1996, 104, 8605. (b) Schreckenbach, Georg, Yosadara Ruiz-Morales, and_Tom Ziegler. J.Phys.Chem A. 1997,101,4121 (c)Ruiz-Morales,Y.; Schreckenbach,G.; Ziegler.T. **Organometallics** 1996, 15, 3920-3923. (d) Ruiz-Morales, Yosadara, Georg Schreckenbach, and Tom Ziegler. **J.Phys.Chem.** 1996,100,3359. (e) Ehlers,A.W.; Ruiz-Morales,Y.; Baerends,E.J.; Ziegler,T. Inorg.Chem. 1007,36,5031. (f)
6. Schreckenbach,G; Ziegler,T. Theor.Chem.Acc. 1998,99,71.

DENSITY FUNCTIONAL THEORY CALCULATION OF MAGNETIC PROPERTIES: IMPROVED FUNCTIONALS AND CURRENT DEPENDENCE.

S.M. Colwell,

Department of Theoretical Chemistry, University of Cambridge.

In order to calculate magnetic properties of molecules using Density Functional Theory it is, in principle, necessary to incorporate the current. Work so far suggests that the effect of the current dependent term is small, and that it is more important to use exchange-correlation functionals that give accurate results for the orbital eigenvalues.

This paper will survey work done recently in Cambridge to test new functionals developed by Tozer and Handy which are optimised for these eigenvalues. It will also consider the effect of the current and the appropriate form of the current dependent functional for molecular densities.

L22

Relativistic calculations of the NMR shielding and

indirect spin-spin coupling tensors

Lucas Visscher[1], Thomas Enevoldsen[2], Trond Saue[3], Hans-Jørgen Aagard Jensen[2],

Jens Oddershede[2] and Gustavo Aucar[4]

1. Department of Chemistry, Vrije Universiteit Amsterdam, De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

2. Department of Chemistry, Odense University, Campusvej 55, DK-5230 Odense M, Denmark

3. IRSAMC – LPQ, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse CEDEX, France

4. Physics Department, Exact Science Faculty; UNNE, Avda. Libertad 5300, Corrientes, Argentina

Abstract

We will discuss application of the 4-component relativistic RPA method to include relativistic effects in the calculation of NMR parameters.

We will first consider the interpretation and evaluation of the DSO contribution in a relativistic formalism. The different approximations introduced are tested in calculations of the spin-spin coupling tensors of the water analogues (H_2O, H_2S, H_2Se and H_2Te).

In a second application we will compare benchmark values for the NMR shieldings and indirect spin-spin coupling tensors of the hydrogen halides with the result of other approaches. Here we find that inclusion of the spin-orbit coupling in a non-relativistic formalism suffices to recover the relativistic effect on the hydogen shieldings but fails to reproduce the much larger effect on the halogen shieldings.

CALCULATIONS OF ELECTRONIC G-SHIFTS BY LINEAR RESPONSE THEORY FOR MULTI-CONFIGURATIONAL SCF WAVE FUNCTIONS

Maria Engström, Boris Minaev, <u>Olav Vahtras</u>, and Hans Ågren

Multiconfiguration linear response theory is applied to the calculation of electronic g-shifts, normally dominated by the second-order energy correction involving spin-orbit and orbital Zeeman effects. Response theory provides an alternative method for evaluating perturbational expressions, where summation over all excited states is achieved implicitly by solving linear systems of equations. Other contributions (diamagnetic and relativistic) are first-order corrections and are evaluated as expectation values. It is demonstrated for a sequence of diatomic molecules with a triplet ground state what experimental agreement can be expected via the related property given by Curl's relation, the spin-rotation constants. Improvements of the present formalism will be discussed in terms of non-variational corrections and London orbitals.

Density functional calculations of ESR parameters in the zero order regular approximation for relativistic effects

Erik van Lenthe, Paul E.S. Wormer and Ad van der Avoird

A method has been developed for the calculations of ESR parameters (g-tensor, hyperfine interaction tensor) of Kramers doublet open shell molecules, which uses the spinor of the unpaired electron of the paramagnetic molecule, obtained from a density functional calculation.

Spin-orbit coupling is taken into account variationally using the recently developed zeroth order regular approximated (ZORA) relativistic equation, available in the Amsterdam Density Functional program package. Relativistic regular approximated expressions for the Zeeman term and hyperfine interaction were derived and implemented in the ADF program, with the use of numerical integration for the calculation of the corresponding matrix elements.

Since this method includes the spin-orbit coupling and other relativistic effects in the SCF calculation, and uses first order perturbation theory for the Zeeman terms in the Hamiltonian, it is not much more expensive than an ordinary SCF calculation on a molecule without external field, and can easily be used for larger molecules.

PERSPECTIVES ON AB INITIO g-TENSOR CALCULATIONS

Gerald H. Lushington

Ohio Supercomputer Center, 1224 Kinnear Road, Columbus OH, USA 43212-1163

ABSTRACT

Significant progress has been made in recent years toward developing viable ab initio techniques for accurate computation of electronic g-tensors for gas phase molecular radicals. Multi reference configuration interaction techniques have been found to yield highly accurate results for small gas phase molecules, consistently reproducing general trends while also getting good quantitative agreement (less the 20% deviation from experiment for larger g-shifts). The main drawback of this approach is its high computational cost, a factor which becomes prohibitive with increasing size and complexity of the system. Much more computationally tenable methods include ROHF and DFT level descriptions, which sacrifice some computational accuracy but generally still reproduce basic trends in g-shifts and bear some quantitative resemblance to experimental values. Many radical systems of interest, however, do not lend themselves well to gas phase analysis and thus are often studied in solution, matrix or solid state environments – conditions under which the valence character of the radical may be appreciably perturbed, leading to significant differences in g-shifts as compared to gas phase. This project surveys methodologies and results for conventional (gas phase) calculations and provides commentary on possible condensed phase effects and the methods that may be applied to their study.

Electron Spin Resonance g Tensor Calculations

Dylan Jayatilaka

Department of Chemistry, The University of Western Australia,
Nedlands 6009, Australia

Until recently, little attention has been given to calculating the g tensor, a basic molecular property for radicals which defines the magnetic moment in an applied external magnetic field.

In this talk I will describe a new way to calculate the g tensor as a derivative of the energy with respect to an applied magnetic field [1]. Interestingly, the method is formally based on *second* derivatives of the *square* of the Zeeman splitting energy. However, the formal expression can be simplified to a first derivative, and then a new Hellmann-Feynman formula for the g tensor can be derived. To get results, a General Hartree Fock (GHF) method is proposed and implemented. The GHF method can deal with the required spin-orbit interactions in a non-perturbative manner.

g tensor elements are calculated for CO^+, CN, MgF, NO_2, NF_2, CO_2^-, O_3^-, OH_2^+, HCO, and H_2CO^+. In most cases, the agreement is within or close to the expected experimental accuracy of 500 ppm for neon matrix data, but there are still some significant discrepancies. The results are in better agreement with configuration interaction (CI) type calculations than density functional theory (DFT) calculations, although the differences are small. The results are significantly different from perturbation theory predictions. It is found that the diamagnetic contributions to the g tensor are not significant to within the experimental errors, if matrix isolation data is used.

The g tensor for $CoCl_4^{2-}$ ion is also studied, to demonstrate that the method can be applied to non-doublet systems.

References

1. "Electron Spin Resonance g Tensors from General Hartree Fock Calculations" D. Jayatilaka, J. Chem. Phys **108**, 7587 (1998).

APPLICATION OF NUCLEAR SHIELDING SURFACES TO THE FUNDAMENTAL UNDERSTANDING OF ADSORPTION AND DIFFUSION IN MICROPOROUS SOLIDS

Cynthia Jameson
University of Illinois at Chicago

The intermolecular chemical shift provides a means by which very detailed questions can be answered towards a fundamental understanding of two basic processes in the many technological applications of microporous materials: adsorption and diffusion. We will demonstrate that the detailed equilibrium properties of physisorbed small molecules and the rates of cage-to-cage migration in zeolites can be observed and quantitatively reproduced by theoretical calculations. Some of the questions which have been answered include: When molecules are adsorbed in a microporous solid at a given loading, what fraction of the cavities have exactly n molecules? Is adsorption of one type of molecule enhanced or diminished by competition with another type? How many molecules of type 2 can be found in those cavities that have exactly n molecules of type 1? How do the type, size, and locations of cations affect the distribution of molecules within a microporous solid? How is the NMR chemical shift affected by confinement with n molecules of another type in a cavity? A zeolite cage provides a model system for the understanding of solvent effects on chemical shifts, for the theoretical investigation of the temperature dependence of medium chemical shifts under constant volume conditions in which very detailed comparisons with experiment may be carried out.

NMR views of Proton Transfer and Hydrogen Bonding

Hans-Heinrich Limbach

*Freie Universität Berlin, Institut für Organische Chemie,
Takustr. 3, D-14195 Berlin, Germany*

The problem of localization and transfer of hydrogen isotopes in hydrogen bonded hetercyclic compounds, acid-base complexes, transition metal hydrides embedded in liquids and solids is a challenging problem of chemistry. In this contribution liquid and solid state NMR - methods are presented which are especially adapted for the study of these problems. For certain model systems kinetic hydrogen/ deuteron/tritium-isotope effects on proton transfer through and across a barrier can be obtained by various methods of dynamic NMR spectroscopy, ranging from the second to the nanosecond timescale. In the case of low-barriers hydrogen bonds H/D-isotope effects on the hydron locations are observed using dipolar solid state NMR which are related to H/D isotope effects on chemical shifts. Novel low-temperature NMR methods allow us to study acid-base interactions in polar solvents. Zero-point energies are directly measured via H/D fractionation factor measurements. For the first time, scalar couplings between heavy atoms of hydrogen bonds are observed which indicate the covalent character of these bonds. All experimental values are used to model theoretically the details of the proton motion in hydrogen bonds.

References

Hydrogen Transfer: Theory and Experiment. Eds. H.H.Limbach and J.Manz. Ber.Bunsenges.Phys.Chem. *102*, March 1998

SOS-DFPT (deMon-NMR) CALCULATIONS FOR ENZYME AND ZEOLITE MODELS

G. VALERIO[1], A. GOURSOT[1], R. VETRIVEL[2],
O. MALKINA[3], V. MALKIN[4], C. WONG[5], M. FLOCK[6,7], H. GUO[8]
AND D. R. SALAHUB[6,8]

[1]UMR 5618 CNRS, École de Chimie, 8, rue de l'École Normale, 34296 Montpellier CÉDEX 5, FRANCE
[2]Catalysis Division, National Chemical Laboratory, Pune 411008, INDIA
[3]Computing Center, Slovak Academy of Sciences, Dubravska cesta 9, 84236 Bratislava, SLOVAKIA
[4]Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dubravska cesta 9, 84236 Bratislava, SLOVAKIA
[5]Mount Sinai School of Medicine, Department of Physiology and Biophysics, New York, NY, 10029-6574 U.S.A.
[6]Département de chimie, Université de Montréal, C.P. 6128, succursale Centre-ville, Montréal, Québec, H3C 3J7, CANADA
[7]Catholic University of Leuven, Department of Chemistry, Celestijnenlaan 200F, 3000 Heverlee-Leuven, BELGIUM
[8]CERCA - CEntre for Research on Computation and its Applications, suite 400, 5160 boul. Décarie, Montréal, Québec H3X 2H9, CANADA

The SOS-DFPT method implemented in the deMon-NMR program has proven to be an efficient and highly accurate source of NMR chemical shifts. Progress will be reported on applications involving complex systems.

• Hydrogen-bonded imidazole complexes were chosen to model the catalytic triad of serine proteases. The focus is on nitrogen atoms as they are known to be extremely sensitive to intermolecular interactions and to the protonation state. The validity of various aspects of the models can be established using SOS-DFPT.

• ^{29}Si and ^{27}Al shifts have been calculated for models of the nine different sites in zeolite-β. The Si shifts for single-T-site models already allow an assignment with a relative error less than 1 ppm and an absolute error of about 5ppm. Two-site models reduce the absolute error to 1 ppm.

ELECTRIC FIELD GRADIENTS IN SOLIDS BY THE FULL-POTENTIAL LAPW METHOD

K. Schwarz and P.Blaha

Technische Universität Wien, A-1060 Vienna, Austria

NMR is one of the experimental techniques to measure electric field gradients (EFGs) by nuclear quadrupole interaction. The EFG is a traceless tensor defined as the second derivative of the electrostatic potential with respect to coordinates. Up to about 10 years ago EFG experiments were often interpreted with a simple point charge model from which the electrostatic potential and thus the EFG is deduced, but Sternheimer antishielding factors were needed to correct for the shortcoming. Modern electronic structure calculations provide among other quantities the electron density distribution from which the EFG can be calculated without further approximations. For solids such calculations are based on density functional theory (DFT) according to Kohn and Sham. The interacting system is mapped in a unique manner onto an effective non-interacting system with the same total density. The effective local one-particle potential consists of a mean-field (Hartee) part and an exchange-correlation part which, in principle, incorporates all correlation effects exactly. However, the exact functional form of this potential is not known and thus one needs to make approximations. The local density approximation (LDA) is often used but recently an improvement, namely the generalized gradient approximation (GGA) has reached (almost) "chemical accuracy".

One among the most accurate schemes for solving the Kohn Sham equations is the full-potential linearized augmented plane wave (LAPW) method. In this method the unit cell is partitioned into (non-overlapping) atomic spheres centered around the atomic sites and an interstitial region, where in the former atomic-like functions and in the latter plane waves are used. In FP-LAPW the potential and charge density are expanded into lattice harmonics (inside each atomic sphere) and in a Fourier series (in the interstitial region) and thus they are completely general. The numerical (radial) wave functions guarantee a very accurate description of the electron density distribution, especially near the nucleus and its anisotropy that leads to the EFG. Application to insulators, metals, magnets, superconductors, etc lead to insight into the origin of EFGs and good agreement with experiments.

A fully relativistic description of the hyperfine interaction in solids

<u>H. Ebert</u>, H. Freyer, M. Deng, and J. Voitländer

Institute for Physical Chemistry, University of Munich, Theresienstr. 37, D-80333 München, Germany

A linear response formalism will be presented that has been developed within the framework of spin-polarized relativistic multiple-scattering theory (SPR-KKR) and the Green's function technique to allow for a calculation of magnetic susceptibilities and Knight-shifts. This very general approach allows to deal with paramagnetic as well as ferromagnetic solids. In addition the approach is suited to deal with all spin and orbital contributions to the magnetic susceptibility and Knight-shift on the same level. Furthermore all relativistic effects are taken properly into account. As a consequence one finds – apart from the conventional orbital Van Vleck-contribution to the susceptibility and Knight-shift – an additional orbital contribution due to the spin-orbit interaction. Applications will be presented for the pure 3d-, 4d- and 5d-transition metals. The extension of the presented scheme to alloys and inhomogeneous systems as for example surfaces is straightforward and will be discussed in short. In addition an analogous fully relativistic treatment of other hyperfine interaction parameters of solids as for example the nuclear spin-lattice relaxation time will be sketched.

The second part of the contribution will be devoted to spontaneously magnetized solids. For the corresponding hyperfine field a proper decomposition of these fields into the conventional Fermi-contact, spin-dipolar and orbital parts will be presented and discussed. In discussing corresponding results, the main emphasis will be laid on the spin-orbit induced orbital contributions to the hyperfine field that are by no means neglectable compared to the dominating Fermi-contact part. Finally results of calculations of the spin-orbit induced electric field gradients in cubic systems will be discussed to demonstrate the symmetry breaking effect of the spin-orbit interaction.

Ab-initio theory of the NMR chemical shifts in solids and liquids

Francesco Mauri

Institut Romand de Recherche Numérique en Physique des Matériaux, PPH-Ecublens, CH-1015 Lausanne, Switzerland

I will present a theory for the ab-initio computation of the NMR chemical shifts in condensed matter systems[1]. The formalism can be applied to periodic crystals or, using a super-cell technique, to liquids and amorphous materials. I will illustrate the method with applications to crystalline and amorphous silica, to amorphous carbon thin films, and to ice and liquid water.

[1] F. Mauri, B. Pfrommer, and S. G. Louie, Phys. Rev. Lett. 77, 5300 (1996).

ISOLATED WATER MOLECULE.
NEW EXPERIMENTAL AND THEORETICAL DATA

N. M. Sergeyev

NMR Laboratory, Department of Chemistry
Moscow State University, 119899, Moscow Russia

During last years new experimental and theoretical results were obtained for NMR parameters of water molecule. Experimental data were obtained for dilute solutions of water in nitromethane where proton exchange is stopped and water can be postulated to exist in monomeric form or as isolated molecules. The H-D coupling constant and ^{17}O-H and ^{17}O-D coupling constants in water were obtained with high accuracy of about 0.01 Hz. This allowed us to find D/H isotope effects on coupling constants and D/H induced 17O isotope shifts. The primary isotope effect on ^{17}O-H coupling constant was found to negative in accord with theoretical estimates. Also a small but significant nonadditivity of D/H isotope effects for ^{17}O chemical shifts was established. Dilute solutions of water in nitromethane also lead to long proton and deuteron relaxation times. For mixtures of H_2O and D_2O the equilibrium constant for the reaction $H_2O + D_2O = 2$ HDO was found using ^{17}O NMR and also a combination of ^{1}H and ^{2}D NMR spectra. Accuracy for experimental and theoretical results is analyzed and the sense of the comparison between experimental and calculated is discussed. At present in some cases calculated NMR parameters for small molecules can be considered as more accurate than the experimental ones. It is worth noting that the isotope effects studies are an important step in checking any theoretical approach as the isotope effects on NMR parameters can be considered as small deviations from the equilibrated values and can be treated in terms of the theory of perturbation.

Isotope effects on the NMR parameters of water calculated from correlated nuclear shielding and nuclear spin-spin coupling surfaces

W.T. Raynes

Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK

Coefficients of the two nuclear shielding surfaces $\sigma(O)$ and $\sigma(H)$ and the two nuclear spin-spin coupling surfaces $J(H,H)$ and $J(O,H)$ of the water molecule have been calculated to second order in internal displacement coordinates using a correlated wavefunction. These coefficients have been used to calculate the effects of isotopic substitutions (^1H, ^2H and ^{16}O, ^{17}O, ^{18}O) on the four NMR parameters over a range of temperature. The results are in excellent agreement with recent experimental measurements on water isotopomers dissolved in "inert" solvents. Analysis of the calculated results shows that bond stretching at first order dominates the nuclear motion corrections, but that both bond stretching and angle bending at second order make substantial contributions. The observed nonadditivity of deuterium substitution on the ^{17}O isotope shift can be largely attributed to second order bending. Some unexpected features of the shielding and spin-spin coupling surfaces of several molecules will also be discussed.

ABSTRACTS

OF

POSTERS

QED THEORY FOR MAGNETIC RESPONSE PROPERTIES IN MOLECULES

RODOLFO H. ROMERO AND GUSTAVO A. AUCAR

ABSTRACT. The current way to include relativistic effects on calculations of magnetic molecular properties are separated in scalar, 2-component or 4-component (full relativistic) based formalism. All of them starts from Dirac, Pauli or Schrodinger schemes and use perturbation theory (or response theory) to include the correction to the energy which is related with the property analyzed. In this communication we present a new formalism which treat quantized magnetic field and second quantized boson and fermion operators; this is done, to our knowledge for the first time. We use perturbation theory applied also on operators. The fine structure constant is used as perturbative parameter. This formalism is applied on NMR-J tensor calculations. We obtain the different contributions to J, i.e., the usual direct and indirect nuclear spin couplings when magnetic fields are assumed as classical. We also get the QED contributions in a natural manner. Relativistic corrections arise when their 4-component implementation is reduced by current methods to two- or one-component expressions.

FACULTAD DE CIENCIAS EXACTAS Y NATURALES Y AGRIMENSURA. UNIVERSIDAD NACIONAL DEL NORDESTE. AVDA. LIBERTAD 5300 (3400) CORRIENTES, ARGENTINA
E-mail address: rhromero@exa.unne.edu.ar, gaa@rec.unne.edu.ar

CALCULATIONS OF NMR PARAMETERS: SOME APPLICATIONS TO LARGE ORGANIC SYSTEMS

Jiří Czernek and Vladimír Sklenář

Laboratory of Biomolecular Structure and Dynamics, Faculty of Science,
Masaryk University, Kotlářská 2, CZ-611 37 Brno, CZECH REPUBLIC,
e-mail czernek@chemi.muni.cz, sklenar@chemi.muni.cz

For large (containing 16 nonhydrogen atoms) organic molecules – 2,3'-, 2,5'-, and 3',5'-anhydrothymidines – chemical shifts were obtained using SOS-DFPT-IGLO[1], UDFT-GIAO[2], and CPHF-GIAO[3] methods. Shielding for both experimental (based on measured coupling constants and subsequent MM optimizations) and RHF/6-31G** geometries was investigated. Rather good agreement with experimental values of ^{13}C (rms deviations of relationships between theoretical and measured[4] data for these methods were 5.5, 5.2, and 6.6 ppm, respectively) and ^1H chemical shifts (0.233, 0.269, and 0.297) will be demonstrated. SOS-DFPT-IGLO method, being the most reliable, was more than 3 times faster than GIAO-based approaches.

SOS-DFPT[5] was employed to calculate selected ^1H – ^1H spin-spin coupling constants in these systems. As will be shown, excellent agreement with experiment can be obtained which facilitates structural studies of anhydrothymidines[4].

REFERENCES

1. V. G. Malkin, O. L. Malkina, L. A. Erikson, and R. D. Salahub, In *Density Functional Calculations*; Vol. 1 of *Theoretical and Computational Chemistry*. Elsevier, 1995.
2. J. R. Cheeseman, G. W. Truck, T. A. Keith, and M. J. Frish, *J. Chem. Phys.* **104**, 5497-5509 (1996).
3. M. Häser, R. Ahlrichs, H. P. Baron, P. Weis, and H. Horn, *Theor. Chim. Acta* **83**, 455-470 (1992).
4. J. Czernek, J. Lang, and V. Sklenář, manuscript in preparation.
5. V.G. Malkin, O.L. Malkina, and D.R. Salahub, *Chem. Phys. Lett.* **221**, 91-99 (1994).

NMR calculations on Hydrogen Bonded Imidazole Complexes- Application to Serine Proteases

Michaela Flock[1,2] and Hung Guo[3] and Chung Wong[4] and Dennis Salahub[2,3]

[1] Laboratory of Quantum Chemistry, University of Leuven, Celestijnenlaan 200 F, B-3001 Heverlee-Leuven, BELGIUM

[2] Dé partement de chimie, Université de Montré al, C.P. 6128, succursale Centre-ville, Montré al, Qué bec, H3C 3J7, CANADA

[3] CERCA-Centre for Research on Computation and its Applications, suite 400, 5160 boul. Dé carie, Montré al, Qué bec, H3X 2H9, CANADA

[4] Mount Sinai School of Medicine, Department of Physiology and Biophysics, New York, NY, 10029-6574 USA

The imidazole ring, which forms the side chain of the amino acid histidine, plays an important role for protein structure stabilisation and is involved in a number of enzymatic reactions, due to its ability to form hydrogen bonds via the two different nitrogen atoms and even to act as acid or base. In serine proteases the imidazole ring is part of the catalytic triad, which consists of the via hydrogen bonds connected side chains of aspartate, histidine, and serine. Proton and nitrogen NMR techniques where applied to gain information about hydrogen bonding and protonation state of the imidazole ring, in order to support one of the proposed catalytic mechanisms.

We studied the nitrogen chemical shifts in neutral and protonated imidazole rings, and in a number of their hydrogen bonded complexes. Furthermore we present the results of our chemical shift calculations on the active site of serine proteases using models of increasing size.

CALCULATION OF DEUTERIUM ISOTOPE EFFECTS ON ^{13}C CHEMICAL SHIFTS IN BENZOCYCLOBUTENE

Z. Glasovac, P. Novak, Z. Meić and M. Eckert-Maksić

Department of Chemistry, Ruđer Bošković Institute, HR-10001 Zagreb, CROATIA

As a part of our investigation of the molecular and electronic structure of benzocyclobutene (**1**)[1] and its derivatives, we report here on the deuterium isotopic effect (DIE) on ^{13}C NMR chemical shifts in **2-5**. The measured DIE values are correlated with changes of net charges on carbon atoms and with changes in isotropic magnetic shielding calculated by using GIAO-B3LYP method employing several basis sets.
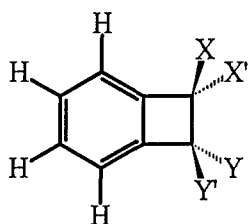
1   X = X' = Y = Y' = H
2   X = D; X' = Y = Y' = H
3   X = X' = D; Y = Y' = H
4   X = Y = D; X' = Y' = H
5   X = X' = Y = Y' = D

Presence of the deuterium was modeled by shortening of the C-D bond distance by 0.012 Å relative to the optimized length in the corresponding C-H bond(s). Theoretical results compare favorably with the experimental data.

---

1. M. Eckert-Maksić, Z. B. Maksić, and M. Klessinger, *J. Chem. Soc., Perkin Trans. 2*, (1994) 285; Z. B. Maksić, M. Eckert-Maksić, M. Hodošček, W. Koch, and D. Kovaček, in: *Molecules in Natural Science and Medicine, An Encomium for Linus Pauling*, Z. B. Maksić and M. Eckert-Maksić (Eds.) Ellis Horwood, Chichester, 1991, p. 333.

Prediction of ^{29}Si MAS NMR chemical shifts in zeolites

P. PULLUMBI[a] , A. GOURSOT[b] , G. VALERIO[b], R. VETRIVEL[b]
and D. R. SALAHUB[d]

(a) Air Liquide, Les Loges en Josas, Jouy en Josas, France
(b) UMR 5618 CNRS, Ecole Nationale Supérieure de Chimie, 8 rue de l'Ecole Normale
34296 Montpellier Cédex 5, France
(c) Catalysis Division, National Chemical Laboratory, 411008 Pune, India
(d) Département de Chimie, Université de Montréal, CP 6128, Succursale Centre Ville,
Montréal, Québec H3C3J7, Canada

^{29}Si NMR chemical shifts have been evaluated from the NMR shielding tensors calculated both within the DFT and HF formalisms. The ^{29}Si NMR chemical shifts have been calculated for the nine crystallographically distinct Si sites of the zeolite-β lattice. The calculations were carried out on cluster models $Si(OSiH_3)_4$ and R_3Si-$OSiR_3$ ($R=OSiH_3$) representing one (1T) and two (2T) sites in the zeolite lattice, respectively. Using the 1T models, the nine signals of the experimental spectrum have been assigned with a relative error of less than 1ppm, the average absolute error being estimated at about 3-5 ppm. The use of a "fragment-averaging" technique based on the results obtained with the 2 T models leads to calculated absolute NMR shifts with an accuracy of $\pm$ 1 ppm for DFT and $\pm$ 2 ppm for HF.

EXPERIMENTAL AND THEORETICAL TENSORS OF ^{31}P AND ^{77}Se NUCLEAR MAGNETIC SHIELDING IN (*neo*Pe-O)$_2$(S)PSeSeP(S)(O-*neo*Pe)$_2$

G. Großmann, D. Scheller, G. Zahn, Dresden University of Technology, Germany

O.L. Malkina, V.G. Malkin, Slovak Academy of Sciences, Bratislava, Slovakia

H. Schmitt, U. Haeberlen, Max-Planck-Institute of Medical Research, Heidelberg, Germany

The *principal values* of P and Se shielding tensors were obtained by Potrzebowski[1] in solid-state MAS NMR investigations of the compound mentioned above. The *orientation of the principal axes* of the tensors with respect to a molecular coordinate system remains hidden by investigations of crystalline powders. This missing information can be obtained by NMR goniometer measurements of a monocrystal or by quantum mechanical nuclear shielding calculations. In this paper we will

- compare the complete experimental and calculated P tensors,
- compare the experimental and calculated principal values of Se tensors,
- try to understand the intensity relations of two NMR signals in the MAS and goniometer spectra.

For this purpose, ^{31}P goniometer NMR spectra of a "monocrystal" were measured and analyzed, SOS-DFPT IGLO calculations of the molecule mentioned were carried out and the crystal structure suggested in the literature[2] as a triclinic one was reinvestigated.

The same conclusions follow from the monocrystal NMR investigation as well as from the SOS-DFPT IGLO calculation: the principal axis *3* deviates only slightly from the P=S direction, the principal axis *2* is nearly perpendicular to the P–Se bond. The intensity relations of the NMR signals can be understood by the presence of a monoclinic phase in addition to the dominant triclinic phase.

---

[1] M. J. Potrzebowski, *Magn. Reson. Chem.* **35**, 8 (1995).

[2] M. J. Potrzebowski, J. Blaszczyk, M. W. Wieczorek, J. Baraniak, W. J. Stec, in press: *Solid State NMR*.

NMR calculations of truly large systems with a simplified DFT-LDA-Tight-Binding scheme

Th. Heine[1,2], G. Seifert[1], and P.W. Fowler[2]

[1] Institut für Theoretische Physik, TU Dresden, D-01062 Dresden, Germany.
[2] Departement of Chemistry, University of Exeter, Exeter, EX4 4QD, UK.

A DFT-LDA Tight Binding (TB-DFT) scheme for calculations of electronic and geometric structure and properties of large molecules, clusters and solids is presented. Atomic-like wave functions as linear combinations of Gaussian type orbitals are used as basis functions. The effective Kohn-Sham (KS) potential is approximated as a superposition of KS-potentials of neutral atoms. Only two-centre matrix elements of the Hamiltonian are considered. Forces on the atoms are calculated either in a semiempirical way under consideration of the electronic states or non empirically using Hellmann-Feynman forces. The small computational effort of this treatment allows to investigate truly large systems up to size of 2000 atoms - including molecular dynamics. An interface allows to use the results - e.g. electronic density, molecular orbitals, Fock and overlap matrices - for property calculations using 'deMon NMR' and 'deMon properties'.

This method is applied for the geometry optimisation and the calculation of chemical shifts of six C_{32} isomers. The results are compared with 'deMon KS3p4/NMR1p1' calculations.

Perturbation theory of magnetic properties and relativistic corrections based on the Lévy-Leblond equation

Alf Chr. Hennum, Trygve Helgaker, and Wim Klopper

Department of Chemistry,

University of Oslo,

P.O.Box 1033 Blindern,

N-0315 OSLO,

Norway

August 10, 1998

Abstract

Relativistic and magnetic corrections are computed using perturbation theory based on the Lévy-Leblond equation — that is, the non-relativistic limit of the Dirac equation — as a zero-order starting point. The theory has been applied through third-order to various electronic states of diatomic one-electron systems (H_2^+, HeH^{2+}, Hg_2^{159+}) and preliminary results for these systems are presented. Effects due to the finite size of the nuclei are also studied.

Analysis of the Effect of Torsion upon NMR Chemical Shieldings and Spin-Spin Coupling Constants in Monosaccharide Me β-D-xylopyranoside. A Density Functional Theory Approach.

M. Hricovíni,[1] O.L. Malkina,[2] F. Bízik,[3] L. Turi Nagy[4] and V.G. Malkin[4]

Institute of Chemistry,[1] Computing Center,[2]
Institute of Virology,[3] Institute of Inorganic Chemistry[4]
Slovak Academy of Sciences, SK-84236 Bratislava, Slovakia

Density functional theory based approaches were used to calculate chemical shieldings and spin-spin coupling constants in a monosaccharide Me β-D-xylopyranoside. Excellent agreement was found between the computed and experimental data for this monosaccharide. Effect of torsion around the C1 - O1 bond showed that chemical shifts of anomeric proton, both ring and O1 oxygens as well as C1, C2 and the methyl carbons strongly depend on the dihedral angle where the changes up to 14 ppm were observed. The variation of chemical shielding of anomeric proton was found to be 0.66 ppm and the analysis revealed that the influence of O1 lone pairs upon its σ values play a crucial role. The computed differences of individual components of the shielding tensors (σ_{ii}) of carbons varied up to 50 ppm. Both one-bond and three-bond proton-carbon coupling constants among anomeric proton, anomeric and methyl carbons [($^1J_{C1-H1}$) and ($^3J_{C(Me)-H1}$)] respectively, showed strong dependence upon the torsion angle Φ. Slight asymmetry, as in case of $^1J_{C1-H1}$ couplings, was observed also in the dependence of $^3J_{C(Me)-H1}$ couplings upon torsion angle Φ. The latter dependence was found comparable with that found experimentally having, however, slightly larger values (~1.5 Hz) of coupling constants close to the synperiplanar conformation.

Reference

Hricovini M., Malkina O.L., Bizik F., Turi Nagy L. and Malkin V.G.
"Calculation of NMR Chemical Shifts and Spin-Spin Coupling Constants in Monosaccharide Me β-D-xylopyranoside Using a Density Functional Theory Approach", J. Phys. Chem. A, 101(1997)9756-9762.

DENSITY FUNCTIONAL APPROACH TO THE STRUCTURES AND EPR PARAMETERS OF IMINOXYL RADICALS

A. R. Jaszewski, S. Berski, J. Jezierska

Faculty of Chemistry, University of Wroclaw, 14 Joliot-Curie St., 50-383 Wroclaw, Poland

Iminoxyls are σ-type radicals characterised by a relatively large isotropic hyperfine coupling constant due to a ^{14}N nucleus ($a_N \approx 30$ G) indicating a significant spin density on nitrogen in an orbital of s-containing type.

The structures and EPR parameters of a set of pyridyl iminoxyl radicals are investigated by the density functional (DFT) approach. All the computations are performed using Becke's three-parametric hybrid exchange functional combined with the Lee-Yang-Parr correlation functional (B3LYP) and the standard 6-31++G(d,p) basis set of Pople.

The molecules under study are $(R)(H)C=N-O\bullet$ iminoxyls, where R = 2-pyridyl, 3-pyridyl and 4-pyridyl. All of them may exist either in E and Z geometry. Model considerations suggest that each isomer of 2-pyridyl and 3-pyridyl iminoxyl radicals has two rotameric forms (syn and anti) differing in the orientation towards the C-C bond linking the $>C=N-O\bullet$ group with a pyridyl ring.

The results of the computations are in good agreement with experimental data and offer a comprehensive picture of isomeric effect on geometric and electronic characteristics (particularly distinct in 2-pyridyl iminoxyl radical through the interaction of the pyridyl nitrogen with the $C=N-O\bullet$ moiety). The calculated isotropic and anisotropic hyperfine coupling constants (hfc) for ^1H and ^{14}N can be used in order to identify a geometric isomer of iminoxyl radicals generated upon inclusion of 2-pyridylaldoxime, 3-pyridylaldoxime and 4-pyridylaldoxime in the channels of thermally activated pentasil zeolite ZSM-5.

The feasibility of this kind of computations for large systems indicate that DFT methods seems to be a useful tool for the study of relationship between structure and spectroscopy properties of large free radicals.

ROVIBRATIONALLY AVERAGED NUCLEAR SHIELDING CONSTANTS IN OCS

Karol Jackowski[1], Michał Jaszuński[2], Włodzimierz Makulski[1] and Juha Vaara[3]

The nuclear shielding constants in OCS are studied using ab initio theoretical methods and gas phase NMR measurements. The shielding surfaces are calculated and the rovibrational effects and the resulting temperature dependence are analyzed. The temperature dependence of ^{13}C shielding in the gas phase is determined experimentally in the range 278—373 K. ^{13}C is the single nucleus for which the experimental data for the temperature dependence can be converted to a reference–independent scale, and good agreement of the measured and calculated ab initio results is observed. For ^{33}S, we discuss a new, more accurate absolute shielding scale.

[1]Department of Chemistry, Warsaw University, 02 093 Warszawa, Pasteura 1, Poland

[2]Institute of Organic Chemistry, Polish Academy of Sciences, 01 224 Warszawa, Kasprzaka 44, Poland e-mail: michaljz@alfa.ichf.edu.pl

[3]Department of Physics and Measurement Technology, Linköping University, S-58 183 Linköping, Sweden and NMR Research Group, Department of Physical Sciences, University of Oulu, FIN-90571 Oulu, Finland

One-bond ^{13}C-^{13}C couplings in diacetylenes; experimental and theoretical studies

Krystyna Kamieńska-Trela[1], Lidia Kania[1], Wojciech Schilf[1], and Irina Balova[2]

1) Institute of Organic Chemistry, Polish Academy of Sciences
Kasprzaka 44, 01-224 Warsaw, Poland

2) Sankt-Petersburg University, Sankt-Petersburg, Russia

Carbon-carbon spin-spin coupling constants across one bond have been measured in several mono and dialkyl substituted diacetylenes, in dialkyl substituted tetraacetylene and in trimethylsilyl substituted diacetylene. This provides new examples of the coupling constants across C_{sp}-C_{sp} single bonds, which, so far, have been determined for a very few compounds only. The semi-empirical INDO FPT calculations have been performed for mono substituted diacetylenes with substituents varying along the first row of the Periodical Table. The calculated results revealed that one-bond ^{13}C-^{13}C coupling constants across C-C triple bonds with the substituent directly bound to the bond concerned as well as those across the central single C-C bond are significantly affected by substituent effects.

„Normal vs. Inverse Halogen Dependence" of NMR Chemical Shifts throughout the Periodic Table. Spin-Orbit Effects and Other Pecularities

Martin Kaupp

Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart

e-mail: kaupp@vsibm1.mpi-stuttgart.mpg.de

We have studied the origins of „normal halogen dependence" (NHD) and „inverse halogen dependence" (IHD) of main group and transition metal NMR chemicals shifts, using DFT-IGLO and DFT-GIAO calculations combined with a recently developed DFT-based perturbation method [1] to compute spin-orbit (SO) corrections. The results are discussed in the light of a recently delineated simple yet general qualitative concept explaining such „SO chemical shifts".[2] The model is based on the observation that the SO-induced spin polarization interacts with the nuclear magnetic moments mainly via a Fermi-contact (FC) term, and thus in part works analogously to the FC mechanism of J-coupling.[2] Examples for this analogy, and for its limits, are demonstrated by explicit DFT calculations of the two quantities. NHD for main group nuclei in the highest oxidation states is generally due to SO effects, transmitted via an effective FC mechanism, due to the significant s-character of the bonding orbitals.[2-4] In contrast, no efficient FC mechanism is available for p-block main group elements in lower oxidation states, as their bonding is dominated by p-orbitals. As a consequence, small SO effects and a tendency towards IHD are found. Similarly, small SO shifts and IHD are computed for early transition metal compounds, due to the predominant d-character of bonding. NHD predominates again for late transition metals. We find this to be due only in part to SO effects. The main reason for the switch from IHD to NHD along the transition metal rows is the different nature of the predominant paramagnetic shielding contributions (involving ligand-to-metal charge transfer couplings for early, metal-to-ligand charge transfer couplings for late transition metals).

[1] V. G. Malkin, O. L. Malkina, D. R. Salahub *Chem. Phys. Lett.* **1996**, *261*, 335.

[2] M. Kaupp, O. L. Malkina, V. G. Malkin, P. Pyykkö, *Chem. Eur. J.* **1998**, *4*, 118.

[3] See, e.g.: M. Kaupp, O. L. Malkina, V. G. Malkin *Chem. Phys. Lett* **1997**, *265*, 55.

[4] See, e.g.: M. Bühl, M. Kaupp, V. G. Malkin, O. L. Malkina *J. Comp. Chem.*, in press.

[5] M. Kaupp, Ch. Aubauer, G. Engelhardt, T. M. Klapötke, O. L. Malkina, submitted.

COMPARISON OF AB INITIO AND EXPERIMENTAL ISOTROPIC HYPERFINE COUPLING CONSTANTS OF VARIOUS SEMIQUINONE RADICAL CATIONS

A.-M. Kelterer[1], M. Sacher[1], D. Niethammer[2], and G.Grampp[1]

[1] Institut für Physikalische und Theoretische Chemie, TU Graz, Austria; [2] Institut für Organische Chemie, FU Berlin, Germany

A number of semiquinone radical cations of different substituted N,N,N',N'-tetraalkyl-p-phenylenediamines (R=Me [1, 2], Et [2, 3, 4], and n-propyl [3]) were investigated experimentally by EPR spectroscopy and theoretically by ab initio computations.

Ab initio calculations were done by UHF/3-21G* and the AM1 method to locate the low energy minima in the potential energy surface. B3LYP/6-31G* density functional theory was used to verify these minima and to calculate the hyperfine coupling constants.

Comparison of experimental values with the B3LYP/6-31G*//UHF/3-21G* calculations show a very good correlation for the TMPPD radical cation, hence this level of theory was used for the other radical cations too. Because of the large number of local minima with the more flexible substituents, the ab initio data are shown only for a small number of local minima.

[1] J. A. Weil, J. R. Bolton, J. E. Wertz, Electron Paramagnetic Resonance, Wiley & Sons, New York, 1994, p. 512.

[2] G. Grampp and G. Stiegler, Z. Phys. Chem, 141 (1984) 185.

[3] M. Sacher, D. Niethammer, A.-M. Kelterer, and G. Grampp, to be published.

[4] J. P. Telo, private communication.

DENSITY FUNCTIONAL CALCULATIONS OF HYPERFINE COUPLING CONSTANTS OF STABLE ALANINE RADICALS

P. Lahorte*, F. De Proft**, B. Masschaele*, P. Cauwels*, W. Langenaeker**, P. Geerlings**, W. Mondelaers*,

*Department of Subatomic and Radiation Physics, University of Gent, Proeftuinstraat 86, B-9000 Gent, BELGIUM **Eenheid Algemene chemie (ALGC), Free University of Brussels, Pleinlaan 2, B-1050 Brussels, BELGIUM

The amino acid alanine is widely accepted as a reference dosimeter on the basis of the concentration of a stable radical which is formed upon irradiation in the solid state with high energy electrons or X-rays. Recent EPR and ENDOR experiments however, suggest the existence of several stable radicals at room temperature.

In this work Density Functional Theory (DFT) calculations (B3LYP functional, variety of Pople basissets) of isotropic hyperfine coupling constants (HFCC's) are performed of both the well-known stable radical and various 'candidate' radicals potentially composing the EPR spectrum of L-alanine. Calculational issues (level of geometry optimisation, basisset quality) affecting the accuracy of the resulting HFCC's are addressed.

Although conclusive answers on the identity of stable radicals in irradiated L-alanine will require further experimental investigation, it is clear that the quality of the calculated coupling constants allows for differentiation between various candidate radicals of different structure and geometry.

The results of this study suggest the usefulness of high level standard quantum chemistry calculations (DFT) in the determination of hyperfine coupling constants in molecules of real scientific and practical interest.

MCSCF LINEAR RESPONSE CALCULATIONS OF CC, CF, AND FF SPIN-SPIN COUPLING TENSORS

Perttu Lantto, Juha Vaara, Jaakko Kaski, and Jukka Jokisaari

NMR Research Group, Department of Physical Sciences, University of Oulu, P.O.Box 333, FIN-90571 Oulu, Finland

In NMR experiments performed in anisotropic phases, the anisotropic part of the indirect KL spin-spin coupling tensor $\mathbf{J}_{KL}$ contributes to the experimental direct dipolar coupling as $D_{KL}^{exp} = D_{KL} + \frac{1}{2} J_{KL}^{aniso}$. The magnitude of J_{KL}^{aniso} should be known if the D_{KL}^{exp} are used in accurate determinations of molecular orientation or geometry.

$\mathbf{J}_{KL}$ poses considerable requirements for basis sets and electron correlation treatment in *ab initio* calculations. We report MCSCF linear response [1] calculations for CC, CF, and FF couplings with all the different physical contributions taken into account. Mostly large restricted active space wave functions and extensive basis sets have been used. The $^nJ_{CC}$ ($n = 1, 2, 3$) couplings have been determined in benzene (C_6H_6) [2] and in simple hydrocarbons C_2H_m ($m = 2, 4, 6$) [3], illustrating the dependence of the coupling on the hybridisation of the carbon atoms. The CF and FF coupling tensors have been calculated in *para*-difluorobenzene ($C_6H_4F_2$) [4] and in the different fluoromethanes CH_kF_{4-k} ($k = 1, 2, 3$) [5].

Unlike in the CC couplings where J_{KL}^{aniso} is negligible, it appears that the indirect contribution to the CF and FF couplings has to be taken into account in the experimental work.

[1] O. Vahtras, H. Ågren, P. Jørgensen, H. J. Aa. Jensen, S. B. Padkjær, and T. Helgaker, J. Chem. Phys. **96**, 6120 (1992).

[2] J. Kaski, J. Vaara, and J. Jokisaari, J. Am. Chem. Soc. **118**, 8879 (1996).

[3] J. Kaski, P. Lantto, J. Vaara, and J. Jokisaari, J. Am. Chem. Soc. **120**, 3993 (1998).

[4] J. Vaara, J. Kaski, and J. Jokisaari, *in preparation*.

[5] P. Lantto, J. Kaski, J. Vaara, and J. Jokisaari, *in preparation*.

Isotope Effects on Structure and Dynamics of Some Radical Cations Studied by Ab Initio and DFT Calculations and ESR Spectroscopy

S. Lunell[1], T. Fängström[1], P. Wang[2] and M. Shiotani[2]

[1]*Department of Quantum Chemistry, Uppsala University, Box 518, S-75120 Uppsala, Sweden*
and
[2]*Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739, Japan*

Deuterium isotope effects on conformation and ESR spectra of some selectively deuterated radical cations are studied using accurate *ab initio* and density functional theory (DFT) quantum chemical methods, and compared with experimental data obtained with matrix-isolation ESR techniques. The temperature dependence of the ESR spectra is studied in the temperature range 4 K – 100 K. The applicability and limitations of different computational methods are illustrated by results on partially deuterated dimethyl ether and cyclohexane radical cations.

Dynamical corrections to proton and muon hyperfine coupling constants: a comparison method for open-shell *ab initio* techniques.

R. M. Macrae[1], T. M. Briere[2]

[1]*Muon Science Laboratory, The Institute of Physical and Chemical Research (RIKEN), 2-1 Hirosawa, Wako-shi, Saitama 351-01, Japan*

[2]*Institute of Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan*

Typical benchmark parameters for *ab initio* theory used in the optimisation of techniques and basis sets are geometry (bond lengths, bond angles) and harmonic vibration frequencies, and other energy parameters such as heat of formation. For open-shell systems, another useful parameter is the "Fermi contact" contribution to the hyperfine interaction, A_X, proportional to the electronic spin density at the nucleus X and normally computed at the radical's calculated equilibrium geometry[?, ?]. Recent studies suggest that the family of density functional methods show great promise for economical evaluation of A_X with a precision comparable to that of CISD or CCSD[?]. However, dynamical corrections, in which the hyperfine parameter is averaged over some thermally-accessible segment of the potential energy surface, greatly alter this picture; in certain cases such as internal rotation around a partial double bond, density functional techniques show themselves to be problematic [?]. The present work presents studies of torsion around a CO partial double bond in α,β-unsaturated α-hydroxyalkyl radicals and their isotopomeric counterparts in which H has been replaced by its *light* isotope, muonium. In general, the best results (in terms of comparison with experiment) are given by the most computationally-expensive techniques, CISD, CCSD, and MP2. Additionally, isotopomeric studies of this kind are demonstrated to be a powerful tool for evaluation of the accuracy of potential energy surfaces and properties derived from the electronic wavefunction.

References

[1] I. Carmichael, *J. Phys. Chem.* **95**, (1991), 108.

[2] D. M. Chipman, I. Carmichael, D. Feller, *J. Phys. Chem.* **95**, (1991), 4702.

[3] B. Engels, L. A. Eriksson, S. Lunell, *Adv. Quantum Chem.* **27**, (1996), 298.

[4] C. H Choi, M. Kertesz, A. Karpfen, *Chem. Phys. Letters* **276**, (1997), 266.

DFT CALCULATIONS OF HYPERFINE COUPLING CONSTANTS FOR TRANSITION METAL COMPOUNDS

Markéta Munzarová[1,2], Martin Kaupp[1] and Pavel Kubáček[2]

1 Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany

2 Department of Theoretical and Physical Chemistry, Faculty of Science, Masaryk University, Kotlárská 2, CZ-611 37 Brno, Czech Republic

e-mails: munzar@vsibm3.mpi-stuttgart.mpg.de, kaupp@vsibm1.mpi-stuttgart.mpg.de, kubacek@sci.muni.cz

The isotropic hyperfine coupling constants (hfcc) for a range of first-row transition metal compounds have been investigated by means of density functional theory. Several gradient-corrected and hybrid functionals have been applied in order to examine their performance for different systems. Basis set effects have also been investigated. A variety of molecules with different sizes and bonding characters were treated, ranging from diatomic oxides, nitrides and halides up to penta- and hexacoordinated carbonyl-, cyano-, and nitrosyl-complexes.

Direct and spin-polarization contributions to the hfcc's have been analyzed for all complexes. Contributions arising from the spin polarization of 2s and 3s orbitals have been found to increase with the number of unpaired electrons in metal d-orbitals. Valence orbital contributions are not as systematic and clearly depend on the s-character of the SOMO(s), they are positive for molecules with no or very weak s-character and negative otherwise.

The effect of different exchange and correlation treatments on the direct and indirect contributions to metal hfcc's has been explored. A proper exchange treatment has been found to be particulary important. Inclusion of HF exchange in hybrid functionals results in more pronounced spin polarizations and, with a few exceptions, in weaker direct contributions. As a consequence, spin densities at the metal become less positive. The general behaviour of different functionals is as follows: B3PW91 gives metal hfcc's very close to experiment for most of the systems treated. Some high-spin molecules with relatively low or zero direct contributions to the hfcc are described substantially better when 50% HF exchange is included in the density functional.

NMR chemical shifts in MNDO approximation: Parameters and results for H, C, N, and O.

S. Patchkovskii[a] and W. Thiel[b]

(a) Dept. of Chemistry, University of Calgary, 2500 University Dr NW, Calgary, AB, T2N 1N4 Canada; (b) Organisch-chemisches Institut, Universität Zürich, Winterthurerstr. 190, CH-8057 Zürich, Switzerland

Evaluation of the NMR chemical shift tensor was implemented at the semiempirical MNDO/d level using gauge-including atomic orbitals and analytical derivative theory. Calculations with standard MNDO parameters overestimate the variation of the paramagnetic contributions. Agreement with experiment is improved by reoptimizing electronic structure parameters to reproduce 290 experimental chemical shift values for 97 small molecules and ions. The reference set covers chemical shift ranges of 31, 346, 933, and 1650 ppm for H, C, N, and O, respectively. Final RMS deviations from experiment are 0.638, 13.6, 39.6, and 80.6 ppm respectively for H, C, N, and O, down from 1.93, 36.8, 120.0, and 119.0 ppm for original MNDO. A significant fraction of the total error is due to small molecules with unusual bonding. On a large set of solution NMR data for 384 common organic molecules, the RMS errors are reduced to 11.9, 38.8, and 61.7 ppm for C,N, and O, respectively. Computed chemical shifts are sensitive to the molecular geometry. Bond lengths accurate to at least 0.05Å are normally required for reasonable agreement with experiment. Three-center terms typically contribute a few ppm to the total chemical shift for all four elements studied and are essential for a qualitatively correct description of ¹H chemical shifts and NICS. These terms are less important for C, N, and O and can usually be omitted without significantly degrading the results. Notable exceptions are molecules with cumulated double bonds and systems with long-range effects due to aromatic rings. The overall quality of the results obtained with the NMR-specific parametrization is competitive with non-correlated *ab initio* calculations.

COMPARATIVE STUDIES OF THE EXPERIMENTAL AND CALCULATED QCC AND MÖSSBAUER SHIFTS FOR THE CENTRAL AND TERMINAL ATOMS IN NON-TRANSITION ELEMENT'S COMPOUNDS

O. Kh. Poleshchuk[1], J. N. Latosińska[2], J. Koput[3]

[1]Department of Chemistry, Tomsk Pedagogical State University, 634041 Tomsk, Russia
[2]Institute of Physics, Adam Mickiewicz University, 61-614 Poznań, Poland
[3]Department of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland

The subject of this paper was analysis of the electron density and populations of the s and p orbitals in inorganic compounds as well as complexes containing such atoms as Sn, Sb, Al, I and Cl with different organic ligands. The use of NQR and Mössbauer spectroscopies enabled simultaneous analysis of changes in the s-and p-orbital electron density occurring upon complex formation. Results were referred to the distributions of electron density calculated by ab initio methods. The calculations were carried out with the program packages GAMESS, MOLCAS, HONDO and GAUSSIAN 94, run on an IBM RS/6000 work station in the double polarised TZ2P basis set. Results were obtained on the HF 4-31G, 6-311G** and ccpVZ levels of the theory. The quadrupole coupling constants for Sn, Sb, Al, I, Cl and Br were calculated on the basis of the eigenvalues of the electric field gradient tensor using Townes-Dailey approximation.

The NQCC constants for the central atoms (Sn, Sb and I) calculated by the program packages HONDO and GAUSSIAN using the extended basis 6-311 G** with pseudo-potential were much lower than the experimental data. Calculations performed by MOLCAS and GAMESS packages using the 4-31G basis set led to NQCC much closer to the experimental ones. The frequencies calculated for the terminal halogen atoms are well correlated with the experimental results in 6-311G** basis. Also, a good agreement with the experiment was obtained for NQCC values calculated for the central atoms of some compounds by the PM3 and AM1 methods using Townes-Dailey approximation. We concluded that application of the pseudo-potential by HONDO and GAUSSIAN packages did not lead to appropriate NQCC values for the non-transition atoms containing many electrons such as Sn, Sb and I. Analysis of the chemical shifts in the Mössbauer spectra of the model complexes (in which the bond lengths between central atom and organic ligand were changed) containing either antimony or tin led to the conclusion that in the case of Sb atoms the shifts were caused by a change in the 5s -orbital population while the shifts attributed to cis-$SnCl_4L_2$ complexes could be related to the shielding of 5p-orbitals. The different behaviour of Sn and Sb is a consequence of a different hypervalency of bonds determined by a greater contribution of electron density coming from the s-orbitals of the central atom in the chemical bond between the ligand and Sn than between the ligand and Sb.

The Electric Field Dependence Of Nuclear Spin-Spin Coupling

M. Grayson and W.T. Raynes

Dept. of Chemistry, The University of Sheffield, Sheffield, S3 7HF, UK

Ab initio calculations of the electric field dependences of nuclear spin-spin coupling have been carried out for the first time. The systems under study include each of several small molecules placed in a uniform electric field. The derivatives of the coupling up to second order in the electric field have been determined. The number of independent coefficients depends on the "site symmetry" of the coupled nuclei in relation to the molecule as a whole. For the case of J(H,H) in molecules such as water and methanal allowance must be made for the exchange symmetry of the proton pair.

Results will be presented for the water molecule and, it is hoped, a number of other small molecules. For water calculations at the SCF and MCSCF levels show, as expected, that electron correlation effects are very important. For example, for the proton-proton coupling $dJ(iso)/dF_z$ is -5.45 Hz $(a.u.)^{-1}$ at the SCF level and + 34.15 Hz $(a.u.)^{-1}$ at the MCSCF level where the z-axis is the C_2 axis. Almost all of this change is due to the effect of electron correlation on the derivative of the Fermi contact term.

Magnetic Field Density Functional Theory

Freddie R. Salsbury, Jr.[†‡], and Robert A. Harris[‡]
[†]Materials Sciences Division, Lawrewnce Berkeley National Laboratory
[‡]Department of Chemistry, University of California, Berkeley

Over the past 2 years an alternative form of density functional theory, Magnetic Field Density Functional Theory (BDFT), has been formulated (1). This theory, in principle, can allow for simpler computation and interpretation of NMR parameters, though much computation work remains to be performed. The basic elements of this theory will be presented.

(1) F. R. Salsbury, and R. A. Harris, *J. Chem. Phys.*, 108 (**15**) 6102 (1998) and references therein.

Determination of Proton Hyperfine Tensors in Single Crystals of *D. vulgaris* Miyazaki F [NiFe] Hydrogenase. Pulsed-ENDOR Spectroscopy and DFT Calculations.

M. Stein, *O. Trofanchuk, M. Brecht, F. Lendzian, Y. Higuchi*[§],
W. Lubitz

Max-Volmer-Institut für Biophysikalische Chemie und Biochemie, Technische Universität Berlin, Strasse des 17. Juni 135, D-10623 Berlin, Germany

[§]Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo, Kyoto 606-01, Japan

By Electron Nuclear Double Resonance (ENDOR) spectroscopy the interactions between electron spin and (ligand) nuclear spins in paramagnetic metal complexes can be determined. The investigation of protein single crystals allows the measurement of complete hyperfine tensors, i.e. isotropic and anisotropic contribution, of the active center of paramagnetic biomolecules. The orientation of the g-tensor in the NiFe cluster of Miyazaki F has already been determined [1]. The "ready" Ni-B state of the [NiFe] hydrogenase of *D. vulgaris* Miyazaki F [2] was investigated in single crystals by X-Band (9.5 GHz) ^{1}H pulsed-ENDOR spectroscopy. We were able to determine the complete hyperfine tensors of three protons in the vicinity of the active center. The analysis of the experimental data gave two proton hyperfine tensors with large isotropic contributions (11 and 10 MHz) and one smaller almost purely dipolar hyperfine interaction ($a_{iso} = 5$ MHz). Based on comparison of the anisotropic dipolar contributions of the respective hyperfine tensors with the X-ray structure the two β-cysteinyl protons of the bridging cysteine Cys549 are assigned to the larger two hyperfine interactions while the third mainly dipolar interaction is assigned to a protonated bridging ligand X, i.e. X=OH$^-$ or SH$^-$. DFT calculations on a large cluster model of the active center support this assignment. The spin density is in agreement with experimental data when the bridging ligand is assumed to be OH$^-$.

Acknowledgement

References

1. Ch. Gessner, O. Trofanchuk, K. Kawagoe, Y. Higuchi, N. Yasuoka, and W. Lubitz 1996. Chem. Phys. Lett. 256: 518.
2. Y. Higuchi, T. Yagi, and N. Yasuoka 1997. Structure 5: 1671.

EXCHANGE BROADENING DEPENDENCE OF EPR SPECTRA ON NITROXIDES' ELECTRONIC STRUCTURE AND MEDIA PROPERTIES

Janez Štrancar, Marjana Nemec, Milan Schara

Josef Stefan Institute, Ljubljana, Slovenia

Nitroxide radicals are widely used spin probes exploring the complexity of biological systems, since their electronic structure and therefore EPR spectra are quite sensitive to the local environmental properties.

In this context we studied the EPR spectra lineshapes influenced by the spin exchange. This is one of the effect arising from electronic structure variation. We varied the type of residue attached on oxyl-piperidin ring, their concentration and the solution media. Three nitroxide labels were inspected - tempo, tempone and glusl in different solutions - water, ethanol and acetone, chosen to cover the whole interval of hyperfine tensor changes.

TEMPO   TEMPONE   GLUSL
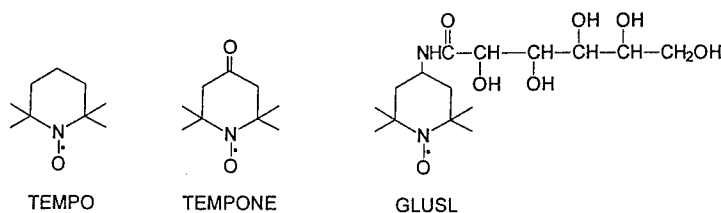
With concentration dependence we measured the exchange frequency which is linearly dependent on the spatial integral of overlapping orbitals. This overlap integral differs by radical type and media polarity due to delocalization of unpaired π electron over piperidine ring.

Temperature dependence was measured to check the effect of dipolar broadening which in case of small nitroxide molecules and therefore fast rotational motions usually vanishes.

We also measured the spectra in the presence of oxygen and without it to exclude the oxygen broadening effect, what is especially important in nonpolar media due to higher oxygen solubility.

The Aromatic Pathway of Chlorins and Porphyrins: A Computational Study

Jonas Jusélius and Dage Sundholm

Department of Chemistry, P.O.Box 55, FIN-00014 Helsinki, Finland

Abstract

The aromatic pathway in chlorins and porphyrins has been studied by performing Hartree-Fock (SCF) calculations of the nuclear magnetic shielding constants using TURBOMOLE [1-2]. The accuracy of the obtained SCF shieldings was checked at second-order Møller-Plesset level. Our calculations show that the preferred aromatic pathway does not include the NH bridge as recently suggested by Cyrañski et al. [4]; instead it forms a classical [18]annulene structure with the NH groups as relatively inert bridging units.

References:
1. R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Letters **1989**, 162, 165.
2. M. Kollwitz, J. Gauss, Chem. Phys. Letters **1996**, 260, 639.
3. M. Kollwitz, J. Gauss, M. Häser, J. Chem. Phys. **1998**, 108, 8295.
4. M.K. Cyrañski, T.M. Krygowski, M. Wisiorowski, N.J.R. van Eikema Hommes, P. von R. Schleyer, Angew. Chem. Int. E.E **1998** 37, 177.

SPIN-ORBIT EFFECTS ON NMR SHIELDING AND SPIN-SPIN COUPLING TENSORS BY QUADRATIC RESPONSE THEORY

J. Vaara,[a] K. Ruud,[b] O. Vahtras,[c] B. Minaev,[c] H. Ågren,[c] and J. Jokisaari[a]

[a]NMR Research Group, Department of Physical Sciences, University of Oulu, P.O. Box 333, FIN-90571 Oulu, Finland
[b]Department of Chemistry, University of Oslo, Blindern, P.O. Box 1033, N-0315 Oslo, Norway
[c]Department of Physics and Measurement Technology, Linköping University, S-58 183 Linköping, Sweden

Due to their importance for the NMR of systems containing heavy elements, the calculation of relativistic effects – the spin-orbit (SO) effect in particular – on NMR parameters has gained significant interest lately. The SO-effect causes the heavy-atom shift of the NMR signals of light nuclei located in the neighbourhood of heavy atoms [1–3]. *Ab initio* methods based on SCF and MCSCF reference states and the quadratic response theory [4] for calculating the SO-corrections to shielding and coupling tensors have recently been developed [5,6]. We discuss the theory in detail and give explicit expressions for the tensor elements. Numerical examples will be provided for the HX and CH_3X (X = F, Cl, Br, I), H_2X (X = O, S, Se, Te), and XeF_2 systems, as well as the bond length dependence of the SO-contribution to ^1H shielding in HI.

[1] Y. Nomura, Y. Takeuchi, and N. Nakagawa, Tetrahedron Lett. **8**, 639 (1969).
[2] P. Pyykkö, A. Görling, and N. Rösch, Mol. Phys. **61**, 195 (1987).
[3] M. Kaupp, O. L. Malkina, V. G. Malkin, and P. Pyykkö, Chem. Eur. J. **4**, 118 (1998).
[4] J. Olsen and P. Jørgensen, J. Chem. Phys. **82**, 3235 (1985).
[5] J. Vaara, K. Ruud, O. Vahtras, H. Ågren, and J. Jokisaari, J. Chem. Phys. **109**, 1212 (1998).
[6] S. Kirpekar, H. J. Aa. Jensen, and J. Oddershede, Theor. Chim. Acta **95**, 35 (1997).

DICHROISM IN THE ELECTROMAGNETIC RESPONSE OF SUPERCONDUCTORS

A. Vetter, E.K.U. Gross

Institut für Theoretische Physik, Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany

A relativistic generalization of the Bogolubov-deGennes equations will be presented where the particle and hole amplitudes are Dirac spinors. In the weakly relativistic limit one obtains, besides the usual spin-orbit, Darwin and kinetic energy corrections, an additional "spin-orbit" and an additional "Darwin" term [1]. The latter terms are present in superconductors only and involve the pairing field in place of the electrostatic potential. In view of the fact that many unconventional superconductors have at least some heavy elements in the lattice, the significance of these new terms for possible superconducting mechanisms in the heavy-fermion and the high-T_c compounds will be discussed.

As a first application, a microsopic theory of dichroism in the magneto-optical properties of superconductors will be presented [2,3]. Four distinct mechanisms for dichroism in superconductors are identified. Two are modifications of mechanisms known from the normal state, and two are novel effects found in superconductors only. The theory is illustrated by numerical calculations for a simple model system. The interplay between relativistic symmetry breaking and superconducting coherence is found to give rise to a variety of new effects, not known from dichroism in the normal state.

[1] K. Capelle, E.K.U. Gross, Phys. Lett. A **198** (1995), 261.
[2] K. Capelle, E.K.U. Gross, B.L. Györffy, Phys. Rev. Lett. **78** (1997), 3753.
[3] K. Capelle, E.K.U. Gross, B.L. Györffy, Phys. Rev. B **58** (1998), 473.

Density Functional Calculations on Sodium Doped Sodium Sodalite

René Windiks, Joachim Sauer

Humboldt-Universität zu Berlin, Institut für Chemie, Arbeitsgruppe Quantenchemie,

Jägerstr. 10/11, D-10117 Berlin, Germany

When dehydrated sodium aluminosilicate sodalite, $(Na^+)_3(AlSiO_4^-)_3$, is doped with sodium atoms, paramagnetic $(Na^+)_4e^- \equiv Na_4^{+3}$ clusters are formed in its cages. Due to the isotropic hyperfine (Fermi contact) interactions the ^{23}Na, ^{27}Al and ^{29}Si MAS NMR spectra show several paramagnetically shifted resonances. The corresponding spin densities at the Si and Al nuclei of the framework and at the Na nuclei of the diamagnetic $(Na^+)_3$ clusters are in the range of 10^{-5} and 10^{-4} atomic units, while at the Na nuclei of the paramagnetic Na_4^{+3} clusters the spin densities are of the order of 10^{-1} atomic units.

We perform density functional calculations to examine the assumption that the observed multiple lines in the ^{27}Al and ^{29}Si NMR spectra are due to the fact that the spin density at a specific T site (T = Al, Si) depends on the number of surrounding paramagnetic Na_4^{+3} clusters [1]. We also rationalize the presence of spin density at the nuclei of the diamagnetic $(Na^+)_3$ clusters.

Calculations are performed on periodic structures as well as on cluster models. The periodic calculations include as many as 88 atoms ($2 \times 1 \times 1$ cells) and employ the DSolid and WIEN95 codes. For the calculations on cluster models it is important that (i) the composition of the models cut out of the periodic structure is similar to the stoichiometric composition of the crystal, (ii) the model is made electrically neutral by adding an array of point charges and (iii) the symmetry of the environment of the magnetic nucleus in the model is the same as in the crystal.

[1] Engelhardt, G.; Feuerstein, M.; Sieger, P.; Markgraber, D.; Stucky, G. Srdanov, V. *J. Chem. Soc. Chem. Commun.* **6**, 729 (1996).

AUTHOR INDEX

LIST

OF

PARTICIPANTS

Gustavo A. **Aucar**
Physics Department
Exact and Natural Science Faculty
Northeastern University
Av. Libertad 5500
3400 Corrientes
Argentina
Phone: +54-783-58460
FAX: +54-783-23968
gaa@rec.unne.edu.ar

Michael **Bühl**
Organisch-Chemisches Institut
Universität Zürich
Winterthurerstr. 190
CH-8057 Zürich
Switzerland
Phone: +41-1-635-4227
FAX: +41-1-635-6836
buehl@oci.unizh.ch

Daniel M. **Chipman**
Radiation Laboratory
University of Notre Dame
Notre Dame, IN 46556
USA
Phone: +219-631-5562
FAX: +219-631-8068
chip@smallv.rad.nd.edu

Jiří **Czernek**
LBSD, Faculty of Sciences,
Masaryk University Brno
Kotlářská 2
CZ-61137 Brno
Czech Republic
Phone: +420-5-411-29380
FAX: +420-5-412-11214
czernek@chemi.muni.cz

Bernd **Engels**
Institut für Phys. und Theor. Chemie
Universität Bonn
D-53115 Bonn
Germany
Phone: +49-228-733-842
FAX: +49-228-739-066
bernd@rs5.thch.uni-bonn.de

Rodney J. **Bartlett**
Quantum Theory Project
University of Florida
PO Box 118435, Gainesville
Florida 32611-8435
USA
Phone: +1-352-392-6974
FAX: +1-352-392-8722
bartlett@qtp.ufl.edu

Beate **Bussemer**
Humboldt University Berlin
Institute of Chemistry
Quantum Chemistry Group
Jägerstrasse 10/11
D-10117 Berlin
Germany
Phone: +49-30-2019-2307
FAX: +49-30-2019-2302
bb@qc.ag-berlin.mpg.de

Susan M. **Colwell**
Department of Theoretical Chemistry
University of Cambridge
Lensfield Road
Cambridge CB2 1EW
U.K.
Phone: +1223-336-535
FAX: +1223-336-362
smc1@cus.cam.ac.uk

Hubert **Ebert**
Inst. für Physik. Chemie
der Universität München
Theresienstr. 37-41
D-80333 München
Germany
Phone: +49-89-2394-4642
FAX: +49-89-2805-248
he@gaia.phys.chemie.uni-muenchen.de

Leif A. **Eriksson**
Department of Quantum Chemistry
Box 518, Uppsala University
75120 Uppsala
Sweden
Phone: +46-18-471-3264
FAX: +46-18-502-402
leifaxel@kvac.uu.se

Richard R. **Ernst**
Lab. für Phys. Chemie
ETH-Zentrum
8092 Zürich
Switzerland
Phone: +41-632-4368
FAX: +41-632-1257
ernst@nmr.phys.chem.ethz.ch

Kai **Exner**
Institut für Organische Chemie und Bioch.
Albertstrasse 21
D-79104 Freiburg i.Br.
Germany
Phone: +49-761-203-6047
FAX: +49-761-203-5987
exner@oce.chemie.uni-freiburg.de

Ulrich **Fleischer**
Department of Chemistry and Biochem.
University of Arkansas
Fayetteville Arkansas 72701
USA
Phone: +1-501-575-5080
FAX: +1-501-575-4049
fleische@uafchem1.uark.edu

Michaela **Flock**
Quantum Chemistry Lab.
University of Leuven
Celestijnenlaan 200 F
3001 Heverlee-Leuven
Belgium
Phone: +32-16-327-384
FAX: +32-16-327-992
Michaela.Flock@chem.kuleuven.ac.be

Gernot **Frenking**
Fachbereich Chemie
Philipps-Universität Marburg
Hans-Meerwein-Strasse
D-35032 Marburg
Germany
Phone: +49-6421-285-563
FAX: +49-6421-282-189
frenking@chemie.uni-marburg.de

Jürgen **Gauss**
Institut für Physikalische Chemie
Universität Mainz
D-55099 Mainz
Germany
Phone: +49-6131-393-736
FAX: +49-6131-393-768
gauss@slater.Chemie.Uni-Mainz.DE

Zoran **Glasovac**
Ruđer Bošković Institute
Dept. of Chemistry, Bijenička c. 54
HR-10001, Zagreb
Croatia
Phone: +385-1-4561-008
FAX: +385-1-4680-185
glasovac@emma.irb.hr

Annick **Goursot**
Ecole de Chimie
8 rue de l'Ecole Normale
34296 Montpellier, Cédex 5
France
Phone: +33-4-6714-4394
FAX: +33-4-6714-4349
goursot@rhodium.enscm.fr

Gisbert **Großmann**
Technische Universität Dresden
Institut für Analytische Chemie
Mommsenstr. 13
D-01062 Dresden
Germany
Phone: +49-351-463-4332
FAX: +49-351-463-2027
Gisbert.Grossmann@chemie.tu-dresden.de

Thomas **Heine**
Institut für Theoretische Physik
Technische Universität Dresden
D-01062 Dresden
Germany
Phone: +49-351-463-5595
FAX: +49-351-463-7297
thomas.heine@physik.tu-dresden.de
T.Heine@exeter.ac.uk

Alf Chr. **Hennum**
Department of Chemistry
University of Oslo
P.O.Box. 1033 Blindern
N-0315 Oslo
Norway
Phone: +47-22-855-430
FAX:
a.c.hennum@kjemi.uio.no

Cynthia J. **Jameson**
University of Illinois at Chicago
60607-761 Chicago, Illinois
USA
Phone: +1-312-996-2352
FAX: +1-312-996-0431
cjj@sigma.chem.uic.edu

Michał **Jaszuński**
Inst. Organic Chemistry
Polish Academy of Sciences
Kasprzaka 44
01-224 Warszawa
Poland
Phone: +48-22-632+0578
FAX: +48-22-632+6681
michaljz@ichf.edu.pl

Krystyna **Kamieńska-Trela**
Institute of Organic Chemistry
Polish Academy of Sciences
Kasprzaka 44
Warsaw 01-224
Poland
Phone: +22-632-32-32-21 ext.2221
FAX: +22-632-66-81
kkt.@.ichf.edu.pl

Martin **Kaupp**
Max-Planck-Institut für Festkörperforschung
Heisenbergstrasse 1
D-70569 Stuttgart
Germany
Phone: +49-711-689-1532
FAX.:   +49-711-689-1010
kaupp@vsibm1.mpi-stuttgart.mpg.de

Miloš **Hricovíni**
Institute of Chemistry
Slovak Academy of Sciences
SK-84238 Bratislava
Slovakia
Phone: +421-7-5941-2754
FAX: +421-7-375-565
chemilos@savba.sk

Adrian R. **Jaszewski**
Department of Chemistry
University of Wroclaw
14 Joliot-Curie street
50 383 Wroclaw
Poland
Phone: +48-71-204-252
FAX: +48-71-328-2348
adrian@wchuwr.chem.uni.wroc.pl

Dylan **Jayatilaka**
Department of Chemistry
University of Western Australia
Nedlands 6009
Australia
Phone: +61-8-9380-3515
FAX: +61-8-9380-1005
dylan@crystal.uwa.edu.au

Shashi P. **Karna**
AFRL/VSSE
3550 Aberdeen Ave, SE
87117-5776 Kirtland AFB, NM
USA
Phone: +1-505-853-3158
FAX: +1-505-846-2290
karnas@ARC.unm.EDU

Anne-Marie **Kelterer**
Institut für Physikal. und Theoret. Chemie
Technical University of Graz
Technikerstr. 4/I
A-8010 Graz
Austria
Phone: +43-316-873-8727
FAX: +43-316-873-8225
kelterer@ptc.tu-graz.ac.at

Werner **Kutzelnigg**
Fakultät für Chemie
Lehrstuhl für Theoretische Chemie
Ruhr-Universität Bochum
D-44780 Bochum
Germany
Phone: +49-234-700-6485
FAX: +49-234-709-4109
Werner.Kutzelnigg@ruhr-uni-bochum.de

Perttu **Lantto**
NMR Research Group
Department of Physical Sciences
University of Oulu
FIN-90571 Oulu
Finland
Phone: +358-8-553-1338
FAX: +358-8-553-1287
Perttu.Lantto@oulu.fi

Patrick M. **Lenahan**
Dept. of Eng. Sciences and Mechanics
The Pennsylvania State University
227 Hammond Bldg.
University Park, PA 16802
USA
Phone: +1-814-863-4630
FAX: +1-814-863-7967
pmlesm@engr.psu.edu

Sten **Lunell**
Department of Quantum Chemistry
Box 518, Uppsala University
75120 Uppsala
Sweden
Phone: +46-18-471-3268
FAX: +46-18-502-402
lunell@Kvac.UU.SE

Roderick M. **Macrae**
Institute of Phys. and
Chem. Research (RIKEN)
2-1 Hirosawa, Wako-shi
Saitama 351-01
Japan
Phone: +81-484-67-9355
FAX: +81-484-62-4648
macrae@rikaxp.riken.go.jp

Philippe **Lahorte**
Department of Subatomic and
Radiation Physics, University of Gent
Proeftuinstraat 86
B-9000 Gent
Belgium
Phone: +32-9-264-6533
FAX: +32-9-264-6699
Philippe.Lahorte@rug.ac.be

Paolo **Lazzeretti**
Dipartimento di Chimica
Università degli Studi
via G. Campi 183
41100 Modena
Italy
Phone: +39-59-378-450
FAX: +39-59-373-543
lazzeret@unimo.it

Hans-Heinrich **Limbach**
Institut für Organische Chemie
Freie Universität Berlin
Takustrasse 3
D-14195 Berlin
Germany
Phone: +49-30-838-5375
FAX: + 49-30-838-5310
limbach@chemie.fu-berlin.de

Gerald H. **Lushington**
Ohio Supercomputer Center
1224 Kinnear Rd
Columbus OH, 43212-1163
USA
Phone: +1-614-292-6036
FAX: +1-614-292-7168
gerald@osc.edu

Vladimir G. **Malkin**
Institute of Inorganic Chemistry
Slovak Academy of Sciences
Dubravska cesta 9
SK-84236 Bratislava
Slovakia
Phone: +421-7-5941-2869
FAX: +421-7-373-541
malkin@savba.sk

Olga L. **Malkina**
Computing Center
Slovak Academy of Sciences
Dubravska cesta 9
SK-84235 Bratislava
Slovakia
Phone: +421-7-375-851
FAX: +421-7-375-881
malkina@savba.sk

Francesco **Mauri**
IRRMA
PPH-Ecublens
CH-1015 Lausanne
Switzerland
Phone: +41-21-693-5428
FAX: +41-21-693-6655
mauri@irrmasg1.epfl.ch

Konstantin M. **Neyman**
Lehrstuhl für Theoretische Chemie
Thechnische Universität München
Lichtenbergstr. 4
D-85747 Garching
Germany
Phone: +49-89-289-13596
FAX: +49-89-289-13622
neyman@theochem.tu-muenchen.de

Serguei **Patchkovskii**
Department of Chemistry
University of Calgary
Calgary, Alberta T2N 1N4
Canada
Phone: +1-403-220-7176
FAX: +1-403-289-9488
patchkov@acs.ucalgary.ca

Peter **Pulay**
Department of Chemistry and Biochem.
University of Arkansas
Fayetteville Arkansas 72701
USA
Phone: +1-501-575-6612
FAX: +1-501-521-7536
pulay@comp.uark.edu

J. **Mareda**
Dept. of Organic Chemistry
University of Geneva
30 quai Ernest-Ansermet
CH-1211 Geneva
Switzerland
Phone: +41-22-702-6099
FAX: +41-22-329-6102
mareda@sc2a.unige.ch

Markéta **Munzarová**
Dept. of Theor. and Physical Chemistry
Faculty of Science, Masaryk University
Kotlárská 2
CZ-611 37 Brno
Czech Republic
Phone: +420-5-4112-9312
FAX: +420-5-4121-1214
munzar@vsibm3.mpi-stuttgart.mpg.de

Patrick **O'Malley**
Department of Chemistry, UMIST
Institute of Sciences and Technology
Sackville Str.
Manchester, M6O 1QD
UK
Phone: +44-161-200-4536
FAX: +44-161-236-7672
patrick@trigger.ch.umist.ac.uk

Oleg Kh. **Poleshchuk**
Institute of Physics
Adam Mickeiwicz University
Umultowska 85
61-614 Poznan
Poland
Phone: +48-61-821-7011 ext. 277
FAX: +48-61-821-7991

Pluton **Pullumbi**
Air Liquide
1 Chemin de la route des Loges
Les Loges-en-Josas, BP 126
Jouy-en-Josas 78354
France
Phone: +33-1-3907-6279
FAX: +33-1-3907-6104
pluton.pullumbi@airliquide.com

Pekka **Pyykkö**
Department of Chemistry
University of Helsinki
POB 55
00014 Helsinki
Finland
Phone: +358-9-1914-0171
FAX: +358-9-1914-0169
pyykko@chem.helsinki.fi

Emil **Roduner**
Institut für Physikalische Chemie
Universität Stuttgart
Pfaffenwaldring 55
D-70569 Stuttgart
Germany
Phone: +49-711-685-4490
FAX: +49-711-685-4495
roduner@indigo01.chemie.uni-stuttgart.de

Dennis R. **Salahub**
Département de chimie
Université de Montréal
C.P. 6128, succursale Centre-ville
Montréal, Québec, H3C 3J7
Canada
Phone: +1-514-343-6755
FAX: +1-514-343-2468
Dennis.Salahub@Umontreal.CA

Karlheinz **Schwarz**
Vienna University of Technology
Theoretical Chemistry
Getreidemarkt 9/158
A-1060 Vienna
Austria
Phone: +43-1-588-01 Ext. 5188
FAX: +43-1-586-8937
kschwarz@email.tuwien.ac.at

Nickolai M. **Sergeyev**
NMR Laboratory
Department of Chemistry
Moscow State University
119899 Moscow
Russia
Phone: +7-095-939-3600
FAX: +7-095-932-8846
nickser@cacr.ioc.ac.ru

William T. **Raynes**
Department of Chemistry
University of Sheffield
Sheffield S3 7HF
United Kingdom
Phone: +44-0-114-222-2000
FAX: +44-0-114-273-8673
W.Raynes@sheffield.ac.uk

Kenneth **Ruud**
Department of Chemistry
University of Oslo
P.O.Box 1033, Blindern
N-0315 Oslo
Norway
Phone: +47 -2285-5432
FAX: +47 -2285-5441
kenneth.ruud@kjemi.uio.no

Fred R. **Salsbury**, Jr
Pines Lab, 11-D62 Hildebrand Hall
Lawrence Berkeley National Laboratory
1 Cyclotron Road
Berkeley CA 94720
USA
Phone: +1-510-486-4875
FAX:
sals@dirac.cchem.berkeley.edu

Daniel **Sebastiani**
Max-Planck-Institut für Festkörperforschung
Heisenbergstrasse 1
D-70569 Stuttgart
Germany
Phone: +49-711-689-1634
FAX: +49-711-678-7224
sebast@prr.mpi-stuttgart.mpg.de

Hans-Ullrich **Siehl**
Abteilung Organische Chemie I
Universität Ulm
D-89069 Ulm
Germany
Phone: +49-731-502-2791
FAX: +49-731-502-2803
ullrich.siehl@chemie.uni-ulm.de

Matthias **Stein**
Max-Volmer-Institut für
Biophysikalische Chemie u. Biochemie
Sekr. PC 14, TU Berlin
Str. des 17. Juni 135
D-10623 Berlin
Germany
Phone: +49-30-314-26500
ms@struktur.chem.tu-berlin.de

Dage **Sundholm**
Department of Chemistry
Helsingfors Universitet
POB 55
FIN-00014 Helsinki
Finland
Phone: +358-9-1914-0176
FAX: +358-9-1914-0169
sundholm@chem.helsinki.fi

Daniel **Tunega**
Institute of Inorganic Chemistry
Slovak Academy of Sciences
Dubravska cesta 9
SK-84236 Bratislava
Slovakia
Phone: +421-7-5941-2667
FAX: +421-7-373-541
uachtuno@savba.sk

Juha **Vaara**
NMR Research Group
Department of Physical Sciences
University of Oulu, P.O.Box 333
FIN-90571 Oulu
Finland
Phone: +358-8-553-1332
FAX: +358-8-553-1287
jvaara@sun3.oulu.fi

Erik **van Lenthe**
Scheikundig Laboratorium
der Vrije Universiteit
1081 HV Amsterdam
The Netherlands
Phone: +31-20-444-7519
FAX: +31-20-444-7643
vlenthe@chem.vu.nl

Janez **Štrancar**
Institute "Jozef Stefan"
Jamova 39
1000 Ljubljana
Slovenia
Phone: +386-61-177-3226
FAX: +386-61-126-3269
janez.strancar@ijs.si

Tomaž **Tekavec**
University of Ljubljana
1000 Ljubljana
Slovenia
Phone: +386-61-224-215
FAX: +386-61-125-4458
tomaz.tekavec@net.zaslon.si

Ladislav **Turi Nagy**
Institute of Inorganic Chemistry
Slovak Academy of Sciences
Dubravska cesta 9
SK-84236 Bratislava
Slovakia
Phone: +421-7-5941-2091
FAX: +421-7-373-541
uachturi@savba.sk

Olav **Vahtras**
Department of Physics (IFM)
Linköping University
SE-581 83 Linköping
Sweden
Phone: +46-13-284-052
Fax: +46-13-132-285
vahtras@ifm.liu.se

Veronique **van Speybroeck**
Department of Subatomic and
Radiation Physics, University of Gent
Proeftuinstraat 86
B-9000 Gent
Belgium
Phone: +32-9-264-6555
FAX: +32-9-264-6699
vero@inwfaxp1.RUG.ac.be

Andreas **Vetter**
Universität Würzburg
Institut für Theoretische Physik
Am Hubland
D-97074 Wuerzburg
Germany
Phone: +49-931-888-5137
FAX: +49-931-888-5141
vetter@physik.uni-wuerzburg.de

Michel **Waroquier**
Department of Subatomic and
Radiation Physics, University of Gent
Proeftuinstraat 86
B-9000 Gent
Belgium
Phone: +32-9-264-6542
FAX: +32-9-264-6699
michel@inwfaxp2.rug.ac.be

Jacques **Weber**
Department of Chemistry
University of Geneva
30 quai Ernest-Ansermet
1211 Geneva 4
Switzerland
Phone: +41-22-702-6530
FAX: +41-22-702-6518
Jacques.Weber@chiphy.unige.ch

Tom **Ziegler**
Department of Chemistry
University of Calgary
Calgary, Alberta T2N 1N4
Canada
Phone: +1-403-220-5368
FAX: +1-403-289-9488
ziegler@acs.ucalgary.ca

Lucas **Visscher**
Department of Chemistry
Vrije Universiteit Amsterdam
De Boelelaan 1083
1081 NL Amsterdam
The Netherlands
Phone: +31-20-444-7519
FAX: +31-20-444-7643
visscher@chem.vu.nl

Roderick E. **Wasylishen**
Department of Chemistry
Dalhousie University, Halifax
Nova Scotia, B3H HJ3
Canada
Phone: +1-902-494-2564
FAX: +1-902-494-1310
RODW@chem1.chem.dal.ca

René **Windiks**
Chemical Institute
Quantum Chemistry Working Group
Humboldt University Berlin
Jägerstr. 10/11
D-10117 Berlin
Germany
Phone: +49-30-20192-306
FAX: +49-30-20192-302
rew@qc.ag-berlin.mpg.de